



**HAL**  
open science

## Recent progress in hydrogen-bonded $\pi$ -conjugated systems displaying Jtype aggregates

Ricardo Nelson, Amparo Ruiz-Carretero

► **To cite this version:**

Ricardo Nelson, Amparo Ruiz-Carretero. Recent progress in hydrogen-bonded  $\pi$ -conjugated systems displaying Jtype aggregates. 2021. <hal-03103362>

**HAL Id: hal-03103362**

**<https://hal.science/hal-03103362v1>**

Preprint submitted on 8 Jan 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



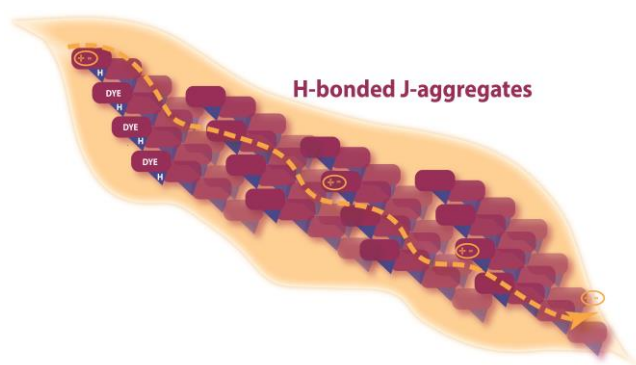
HAL Authorization

# Recent progress in hydrogen-bonded $\pi$ -conjugated systems displaying J-type aggregates

Nelson Ricardo Ávila-Rovelo<sup>a</sup>  
Amparo Ruiz-Carretero<sup>\*a</sup>

<sup>a</sup>University of Strasbourg, CNRS, Institute Charles Sadron, 23  
Rue du Loess, BP 84047, 67034 Strasbourg, Cedex 2, France.  
Phone: 0033-(0)388414178

amparo.ruiz@ics-cnrs.unistra.fr



**Abstract** Supramolecular approaches are of great interest in the design of functional materials. The types of aggregates arising from different noncovalent interactions provide the materials with intriguing properties. In this sense, J-type aggregates are very attractive due to their unique optical properties and capacity to transport excitons. These features make them great candidates in the design of materials for organic electronic devices. Furthermore, the incorporation of additional hydrogen-bonding functionalities provides J-aggregates with superior directionality and connection among the different  $\pi$ -conjugated cores. The control over the formation of H-bonds to achieve functional aggregates is therefore, a promising strategy towards controlled structures with specific functions. This review outlines the most relevant and recent works of  $\pi$ -conjugated systems exhibiting J-type aggregates resulting from hydrogen-bonding interactions. Different types of hydrogen-bonding functionalities will be discussed together with their role in the aggregate properties, their impact in the optoelectronic properties, the self-assembly mechanism and their applications in organic electronics.

## 1. Introduction

### 2. Excitonic properties of J-aggregates

### 3. Amide-containing systems

### 4. Peptide-chromophore systems

### 5. Urea-containing systems

### 6. Systems with complementary H-bonds

### 7. Systems with other H-bonding functionalities

### 8. Conclusions

**Key words** Hydrogen-bonding, J-aggregates, Organic electronics

## 1. Introduction

Intermolecular interactions guide the formation of supramolecular structures with intriguing properties and functions.[1–5] Among the many weak intermolecular interactions found in organic materials, hydrogen bonds (H-bonds) provide directionality and selectivity to the supramolecular assemblies.[6–8] Regarding organic semiconductors,  $\pi$ - $\pi$  stacking interactions are predominant due to the presence of aromatic moieties within their molecular structures. Nevertheless, when H-bonds are also incorporated in the semiconductors, different aggregates can arise from the interplay between  $\pi$ - $\pi$  stacking and H-bonding, making great

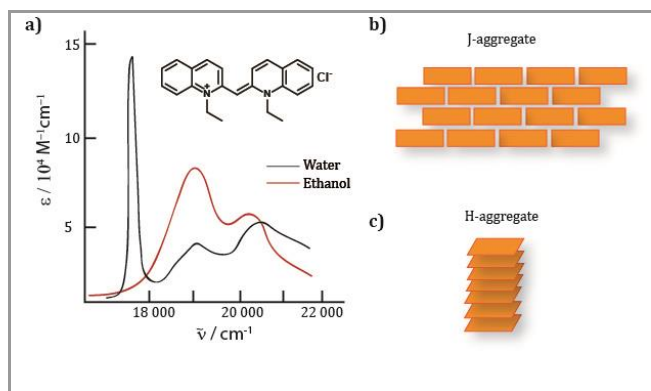
impact on the optoelectronic properties.[9–11] In this sense, J-type aggregates, called like this after one of their first discoverers (Edwin E. Jelley),[12] are very interesting due to their exciting optical properties, very different from the properties of the monomers.

J-type aggregates were initially reported by Günter Scheibe[13] and Edwin E. Jelley[12] in the 1930's as a particular aggregation form of chromophores, where the appearance of an additional, narrow absorption band, bathochromically-shifted with respect to the monomer absorption band with narrow fluorescence band and small Stokes shift was observed (Figure 1a). This behavior was initially found in aqueous solutions of 1,1'-diethyl-2,2'-cyanine chloride abbreviated as PIC (Figure 1a). Scheibe interpreted this result as the polymerization of the dye, meaning supramolecular polymerization due to noncovalent interactions.

Even though different models for the arrangement of dyes within a J-aggregate have been proposed, it is generally accepted that the dyes are usually positioned in a "brick-work" fashion where dyes are significantly slipped with respect to each other, rather than in a face-to-face disposition (Figure 1b).[14] This is necessary to obtain efficient coupling of the transition dipole moments among neighboring molecules.

On the other hand, aggregates showing hypsochromically-shifted absorption bands, with respect to the monomer absorption, are called H-aggregates (from hypsochromic) and usually characterized by low or no fluorescence.[15] In this case, the molecules are stacked in a face-to-face manner, resulting in emission quenching (Figure 1c).

The interesting optical properties of the PIC dye in its aggregated state were revealed when it was applied as spectral sensitizer in photography.[16] Sensitizing dyes are physically adsorbed on silver halides, forming J-aggregates that make possible the migration of an excited dye molecule until it finds a suitable place for charge separation and electron transfer.



**Figure 1** a) PIC chloride molecular structure and the spectroscopic changes from ethanol to water solution, showing the typical J-aggregate red-shifted band. b) Brick-work disposition of dyes within J-aggregates. c) Face-to-face stacks of molecules in H-aggregates.

After the discovery of J-type aggregates in PIC chloride, many other dyes exhibiting the same kind of aggregates have been studied, including merocyanines,[17] squarines,[18] perylene bisimides,[15,19,20] porphyrines,[21] tetrathiofulvalenes[22] and diketopyrrolopyrroles,[9,23] among others. J-type aggregates can be found in assemblies of dyes formed via different noncovalent interactions, even though in this review the most recent and relevant cases of H-bonded synthetic  $\pi$ -conjugated systems displaying J-type aggregates will be discussed. Nevertheless, not only J-type aggregates have been studied in synthetic dyes, they are also found in natural light-harvesting (LH) complexes.[24] This is the case for example, of chlorosome LH complexes found in photosynthetic bacteria, where arrays of bacteriochlorophyll (BChl) derivatives are arranged via H-bonding, metal-ligand coordination and  $\pi$ - $\pi$  stacking to form dye assemblies displaying J-type excitonic coupling.[25] Inspiration from these systems has been crucial to understand the properties of J-type aggregates and extend the studies to synthetic dyes. One of the most studied biomimicking LH complexes uses meso-tetrakis(4-sulfonatophenyl)porphine (TPPS),[26] that by changing the pH has the ability to self-assemble into J- and H-type aggregates. At low pH (<2) TPPS forms J-aggregates forming nanorods that are 3-5 nm in height and reach 50-2000 nm in length, where charges can be efficiently transported.

This review is not meant to be an exhaustive work on J-type aggregates but more to collect the most relevant and recent progress on systems where such types of aggregates arise from H-bonding interactions. The interesting optoelectronic properties and their applications in organic electronics will be reviewed. Since the focus of this review is on H-bonded systems and electronic applications, the reader is guided to broader and more exhaustive reviews on J-type aggregates.[15,27,28]

## 2. Excitonic properties of J-aggregates

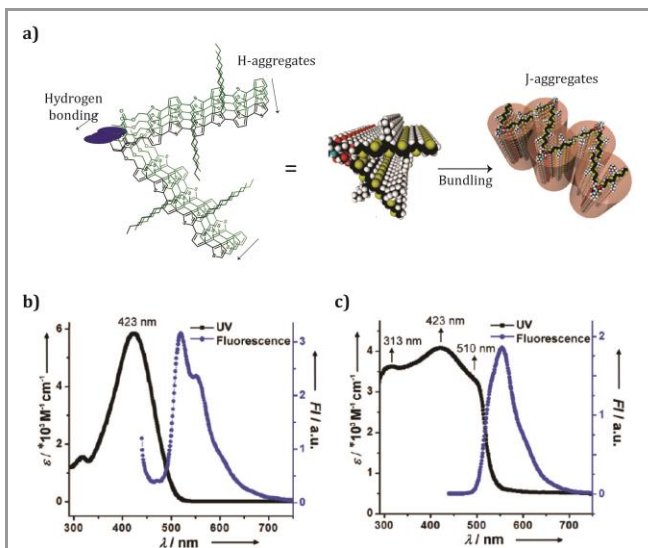
J-aggregates are very attractive due to their unique optical properties and capacity to transport excitons. Since it was discovered that LH complexes in natural photosynthetic organisms and plants are directed by processes similar to those happening in synthetic dyes, the interest in the properties of self-assembled  $\pi$ -conjugated systems has increased. Excited states in J-type aggregates are Frenkel excitons (excitations where hole and electron are tightly

bound)[29,30] delocalized over many dye molecules (up to 50 to 100) depending on the conditions (morphology, disorder and temperature).[31,32] Such delocalization facilitates energy migration within the aggregate, making  $\pi$ -conjugated systems forming J-aggregates great candidates to be used in energy-related materials. Many experimental and theoretical studies have been done on the dimensionality and morphology of J-aggregates in order to know the coherence length and the number of chromophores among which the excitons can be delocalized,[14,31,33,34] finding that it is possible to reach up to 70-100 nm.[35] Such studies show that highly organized self-assembled systems can be the next generation of organic materials for solar cell applications and organic electronics in general. Even though initial studies were done in polar solvents with high salt concentrations to promote the formation of aggregates, many examples of aggregates formed in apolar solvents have been described, being these cases the most interesting for organic electronics purposes. The incorporation of additional H-bonding functionalities provides the aggregates with superior directionality and connection among the different  $\pi$ -cores. The control over the formation of H-bonds to achieve functional aggregates is therefore, a promising strategy towards controlled structures with specific functions.

## 3. Amide-containing systems

Amide functional groups are probably the best known H-bonding forming groups.[36] The well-known synthetic procedures to introduce them into any type of molecule, and their easy characterization by spectroscopy techniques, such as infrared, make them the perfect candidates to study self-assembly processes. Conjugated systems containing one or two amide bonds will be discussed in this part of the review. Stupp *et al.*[37] have shown a hairpin-shaped molecule containing a sexithiophene unit as the electroactive segment attached to a *trans*-1,2-diamidocyclohexane (DACH), as the self-assembly motif (Figure 2a). In this case, the coexistence of H- and J-aggregates results in the broadening of the wavelength spectral range of optical absorption, and in the formation of semiconducting nanowires (Figure 2a). The authors compared the UV-Vis spectra of the hairpin-shaped molecule in toluene straight after solution (fresh) and after 48 hours of aging, finding striking differences in the absorption properties. In addition to the original absorption band at  $\lambda = 423$  nm (Figure 2b), a red-shifted band at 500 nm appeared, while another band previously present at 313 nm become more predominant (Figure 2b and 2c). Organic field effect transistors (OFETs) were fabricated with the hairpin-shaped molecule to evaluate the charge mobility. The hole mobility ( $\mu_h$ ) values found in devices fabricated from toluene solutions (self-assembly promoting solvent) were roughly one order of magnitude higher ( $\mu = 3.46 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) than the values found when the devices were made from non-assembling solvents, such as chlorobenzene and *o*-chlorobenzene ( $\mu = 9.42 \times 10^{-7} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and  $\mu = 1.79 \times 10^{-7} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively). These results could be explained by the broadening of the absorption due to the H- and J-type aggregates that facilitate charge transport along the nanowires and between nanowires. In a following work, the same group reported the applications of the hairpin-shaped derivative in organic photovoltaic devices.[38] In this case, the hairpin-shaped sexithiophene derivative was used as donor

material in bulk heterojunction solar cells in combination with phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the acceptor material. The grooved nature of the hairpin-shaped molecule allows the interaction with PC<sub>61</sub>BM derivatives in a receptor-ligand manner. The authors found J-type aggregates led the formation of bundles of hairpin nanofibers. The J-aggregate signals disappeared upon interaction with PC<sub>61</sub>BM molecules as a proof of the disentanglement of nanofibers upon interaction with the acceptor molecules. Similar results were observed by Ghosh *et al.*[39] They found Davydov splitting[30] in a diketopyrrolopyrrole (DPP) system symmetrically functionalized with amide bonds (Figure 3a). The authors observed the presence of H- and J-type aggregates upon self-assembly conditions.[39] Dilute solutions in chloroform and toluene showed absorption spectra of the monomeric species of DPP-Amide (Figure 3b, blue spectrum), exhibiting two main absorption bands, one at 428 nm, corresponding to a  $\pi$ - $\pi^*$  transition, and a broad band with maxima at 628 nm, attributed to intermolecular charge transfer between the electron-rich (oligothiophene) part of the molecule to the electron-poor (DPP). In contrast, under aggregation conditions, the absorption spectrum differs from the one at low concentration. In this case, new bands appear at higher and lower energies, being H- and J-type aggregates, respectively, and achieving spectral coverage in the visible region and transparency in the near infrared (NIR) region (Figure 3b, pink spectrum). As a proof of concept, the authors fabricated a self-standing PDMS (poly(dimethylsiloxane)) NIR transmitting optical filter by blending DPP-Amide self-assembled fibers at different concentrations. The authors successfully demonstrated the use of the filters in night vision, anticounterfeiting and forensic applications.



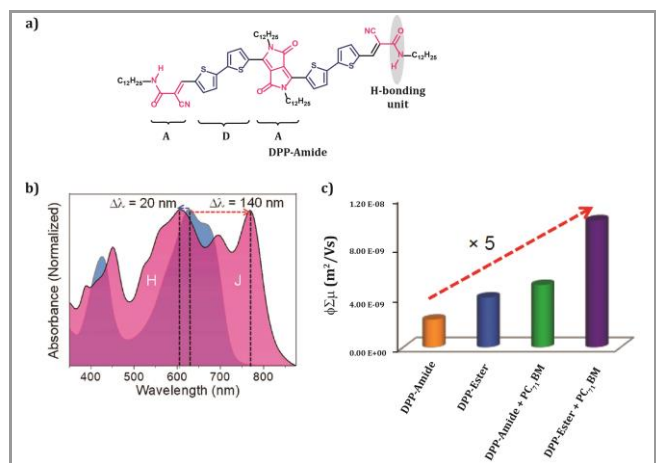
**Figure 2** a) Schematic representation of the self-assembly process of the hairpin-shaped sexithiophene derivative forming H- and J-type aggregates. b) Absorption and emission spectra of the hairpin molecule freshly prepared. c) Absorption and emission spectra of the hairpin molecule after 48 hours aging in toluene. Adapted with permission from (Tsai W-W, Tevis ID, Tayi AS, Cui H, Stupp SI. Semiconducting Nanowires from Hairpin-Shaped Self-Assembling Sexithiophenes. *J Phys Chem B* 2010; 114: 14778–14786). Copyright (2010)

Subsequently, DPP-Amide was studied in combination with PC<sub>71</sub>BM in hybrid organogels exhibiting high

photoconductivity.[40] The DPP-Amide exhibits photoinduced electron transfer only in the assembled state in presence of PC<sub>71</sub>BM leading to enhanced photoconductivity. DPP-Amide only showed photoconductivity in the assembled state, finding a 5-time fold enhancement when blended with PC<sub>71</sub>BM (Figure 3c). An analogue derivative containing ester groups was synthesized as a control molecule (DPP-Ester), which did not show J-aggregates and did not form organogels. The photoconductivity values for DPP-Ester were slightly higher than for DPP-Amide, but when DPP-Ester was blended with PC<sub>71</sub>BM the photoconductivity value did not change. This result highlights the important role of having H-bonds in the molecular structure that result in J-aggregates leading to higher photoconductivity.

The field of perovskite photovoltaic devices has also benefitted from the presence of materials showing J-aggregates. For instance, Kaneko *et al.*[41] have shown H-bonded tetrathiofulvalene (TTF) derivatives containing amide groups that have been used as dopant-free hole transport materials in perovskite solar cells. In this case, the H-bonded TTF derivatives had electrical conductivity values higher than spiro-OMeTAD

(2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene, which is the most usual hole transport material. J-type aggregates were found in H-bonded TTF thin films leading to the formation of nanofibers with enhanced mobility.



**Figure 3** a) Molecular structure of DPP-A. b) Absorption spectra of DPP-A in its disassembled (blue) and assembled (pink) state. c) Photoconductivity values of DPP-A, DPP-Ester and their blends with PC<sub>71</sub>BM. Adapted with permissions from (Ghosh S, Cherumukil S, Suresh CH, Ajayaghosh A. A Supramolecular Nanocomposite as a Near-Infrared-Transmitting Optical Filter for Security and Forensic Applications. *Adv Mater* 2017; 29: 1703783). Copyright (2017) and (Ghosh S, Das S, Saeki A, Praveen VK, Seki S, Ajayaghosh A. A Hybrid Organogel of a Low Band Gap Diketopyrrolopyrrole with PC<sub>71</sub>BM: Phase Separated Morphology and Enhanced Photoconductivity. *ChemNanoMat* 2018; 4: 831–836). Copyright (2018).

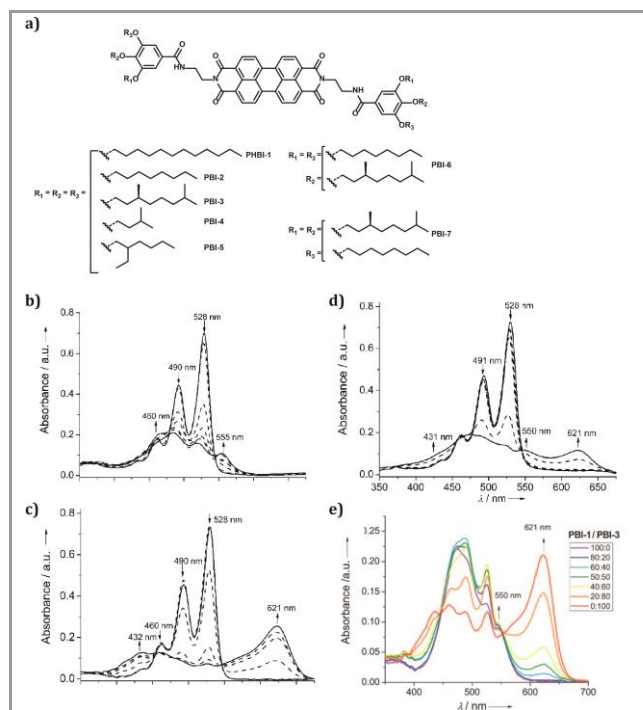
Many examples of PBI derivatives with pending amide groups exhibiting J-aggregates have been reported. The Würthner group has shown multiple examples of self-assembled PBIs[42] containing amide bonds as well as other self-assembly motifs. Back in 2008 they showed a study on how to control H- and J-type homo- and heteroaggregates in amide-containing PBIs. For this purpose, they synthesized several PBI derivatives (Figure 4a) with the same core and amide groups as H-bonding motifs and changed the alkyl chains.[43] The authors found that the steric effects in the peripheral side

chains dictated the self-assembly mode, going from the usually found H-type to the J-type aggregates. **PBIs** containing linear alkyl side chains, which are sterically less demanding, formed face-to-face H-type aggregates (Figure 4b), while the **PBIs** having branched alkyl tails, formed slipped J-aggregates (Figure 4c and 4d) or did not aggregate. The self-assembly studies were performed using mixtures of good and bad solvents, being chloroform and methyl cyclohexane (MCH) in this case. When the amount of MCH increased, the signature for H- or J-type aggregate increased as well. This work also shows mixtures of **PBIs** prone to form H- or J-aggregates, as for example **PBI-1** and **PBI-3** (Figure 4e). In this case, coaggregation in H-type stacks with alternate packing of both chromophores was observed when having a big amount of the H-aggregating **PBI-1**. On the other hand, self-sorting of **PBI-1** and **PBI-3** was observed when having high content of J-aggregate forming **PBI-3**. These results are very relevant to help in the design of photovoltaic devices, for example, where highly organized arrays of donor and acceptor materials are needed. More recently, Wagner *et al.* have shown a similar **PBI** system modified with 1,7-dimethoxy substituents in the bay positions.[44] The authors used this **PBI** derivative to study living supramolecular polymerization, achieving fluorescent J-type aggregates. In previous works, the authors used similar chemical designs without modifying the bay area.[45,46] The modifications on the bay area result in slightly core-twisted **PBIs** that self-assemble into metastable H-aggregates, that are transformed into thermodynamically stable fluorescent J-aggregates by seed-induced living supramolecular polymerization. The control over the supramolecular polymerization is very interesting for the design of functional supramolecular polymers and to study charge carrier transport processes. Not only **PBI** derivatives functionalized with amide bonds have been used to study seeded polymerization where J-type aggregates play an important role. Very recently, Ogi *et al.*[47] have reported a study of seeded polymerization in aqueous media of a **DPP** derivative with pending amide functionalities from the lactam rings. The authors managed to control the polymerization and the morphology of the aggregates, finding 1D fibers exhibiting J-type aggregation.

#### 4. Peptide-chromophore systems

Oligopeptides, containing several amide bonds, are versatile building blocks to program organized structures of  $\pi$ -conjugated molecules[48] The study of natural and artificial self-assembled peptide structures have provided some design rules that allow the control on the morphology and function of peptide-based materials with interesting electronic properties.[49] Together with the peptide sequences, the secondary structures play a major role in the final functions. Furthermore, there are systems described where the  $\pi$ -conjugated segments are embedded within the oligopeptide structure, and oligopeptide systems terminally functionalized with the  $\pi$ -conjugated molecules in case the peptides are covalently linked to the chromophores. For instance, Sun *et al.*[50] reported an oligopeptide of sequence LLKK functionalized with anthracene as the  $\pi$ -conjugated part (Figure 5a). The amino acid sequence was chosen due to its known  $\beta$ -sheet forming tendency that guides the formation of 1D structures. Anthracene was selected because it is known to

form anisotropic assemblies via  $\pi$ -stacking. Self-assembled structures were achieved by casting saturated benzene solutions of the oligopeptide on silicon substrates. 1D fiber-like nanostructures were observed with microscopy techniques and subsequently studied by spectroscopy. The oligopeptide-anthracene in solid state presented red-shifted emission (Figure 5b) and shorter excited state lifetime with respect to

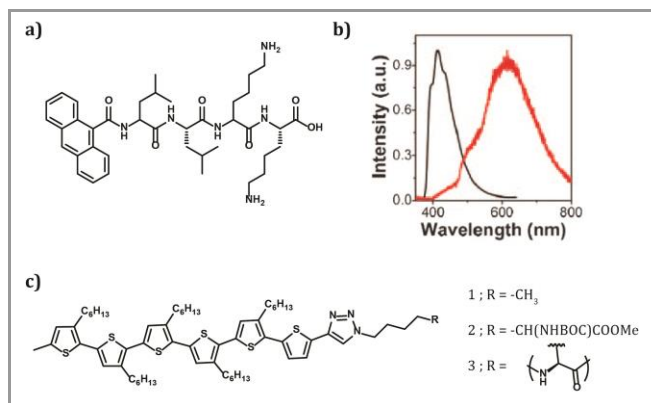


**Figure 4** a) Molecular structure of **PBI-1-7**. Solvent-dependent (in various MCH/CHCl<sub>3</sub> mixtures) UV-visible absorption spectra of b) **PBI-1** (50:50 to 80:20), c) **PBI-4** (40:60 to 70:30), and d) **PBI-7** (50:50 to 90:10) at a concentration of  $1 \times 10^{-5}$  M at 25 °C. Arrows indicate the spectral changes upon increasing the amount of MCH (from 40 to 90%). e) UV-visible absorption spectra of a mixture of **PBI-1** and **PBI-3** in different ratios in 80:20 MCH/CHCl<sub>3</sub> at 25 °C. The total concentration of chromophores remains constant ( $1 \times 10^{-5}$  M) in each mixture. Adapted with permission from (Ghosh S, Li X-Q, Stepanenko V, Würthner F. Control of H- and J-Type  $\pi$  Stacking by Peripheral Alkyl Chains and Self-Sorting Phenomena in Perylene Bisimide Homo- and Heteroaggregates. *Chem – Eur J* 2008; 14: 11343–11357). Copyright 2008.

the oligopeptide-anthracene in water solution. These results confirm the presence of J-type aggregates between the anthracene dyes guided by H-bonding, enhancing electronic communication. The authors fabricated nanoelectronic devices to provide a direct conductivity measurement, achieving conductivity values several orders of magnitude higher than in bulk anthracene. Kumar *et al.*[51] have shown a sexithiophene electroactive segment attached to the side chain of L-lysine that was subsequently polymerized (Figure 5c). The self-assembly properties of the system were studied as well as the optoelectronic properties and the fabrication of photovoltaic devices and organic field effect transistors (OFETs). The results were compared to a protected amino acid and an achiral amino acid non-polymerized (Figure 5c). Thin films were cast from solutions of the three derivatives studied and they all showed red-shifted absorption and formed J-type aggregates. The polymerized derivative forms an  $\alpha$ -helix secondary structure, while the control molecules do not form any helical structure and do not display any circular dichroism signals. Organic solar

cells and OFETs were fabricated with the three derivatives, finding that the oligopeptide forming an  $\alpha$ -helix showed enhanced efficiency in solar cells as well as being the only compound of the three presenting hole mobility. The results point out that the assembly of  $\alpha$ -helically templated chromophores, leads to interconnected networks for charge transport. Other works have used peptides to direct the assembly of porphyrins. For example, Jintoku *et al.*[52] have found that pyridylated C60 interacts with zinc porphyrins functionalized with L-glutamide when they are assembled in J-aggregates. The interaction between the porphyrin and the modified C60 changes the morphology of the porphyrin's assemblies from entangled fibers to vesicles.

Apart from covalently coupling peptides to chromophores, noncovalent approaches where the peptides assemblies guide the organization of chromophores have been pursued. For instance, Koti *et al.*[53] have shown the J-aggregation of **TPPS** guided by polylysine. The concentration of lysine residues needed to induce J-aggregate formation was demonstrated to be three orders of magnitude lower than when monomeric lysine is used. In this case, chirality is transferred from the polypeptide to the porphyrin complex, which is achiral, achieving rod-like structures with J-aggregation of several hundreds of nanometers.



**Figure 5** a) Chemical structure of the LLKK-anthracene derivative. b) Emission spectra of the LLKK-anthracene derivative in an aqueous solution (black) and as 1D, self-assembled structures (red, the assembled structures were measured as solid with a confocal microscope). c) Chemical structure of the L-lysine-sexithiophene derivative. Adapted with permissions of (Sun Y, Jiang L, Schuermann KC, Adriaens W, Zhang L, Boey FYC, De Cola L, Brunsveld L, Chen X. Semiconductive, One-Dimensional, Self-Assembled Nanostructures Based on Oligopeptides with  $\pi$ -Conjugated Segments. *Chem - Eur J* 2011; 17: 4746–4749). Copyright (2011) and (Kumar RJ, MacDonald JM, Singh TB, Waddington LJ, Holmes AB. Hierarchical Self-Assembly of Semiconductor Functionalized Peptide  $\alpha$ -Helices and Optoelectronic Properties. *J Am Chem Soc* 2011; 133: 8564–8573). Copyright (2011).

Short peptides have also been studied to mimic LH complexes. The Park's group has sown nanotube-forming peptides based on L-Phe-L-Phe (FF) systems[54] that incorporate hydrophobic porphyrin chromophores in the nanotubes. The optical spectra showed that the porphyrin dyes were assembled into J-aggregates, resulting in strong exciton coupling between the porphyrin monomers. Apart from porphyrin derivatives, ruthenium chromophores have been successfully immobilized on the surfaces of **FF** nanotubes and derivatives of **FF** peptides, such as **Fmoc-FF**. **Fmoc-FF** forms hydrogels with  $\beta$ -sheet secondary structure that is stable after co-assembly with either ruthenium complexes or porphyrin derivatives. In all cases, the

incorporated chromophores self-assemble into large J-type aggregates with strong exciton coupling.[55–57]

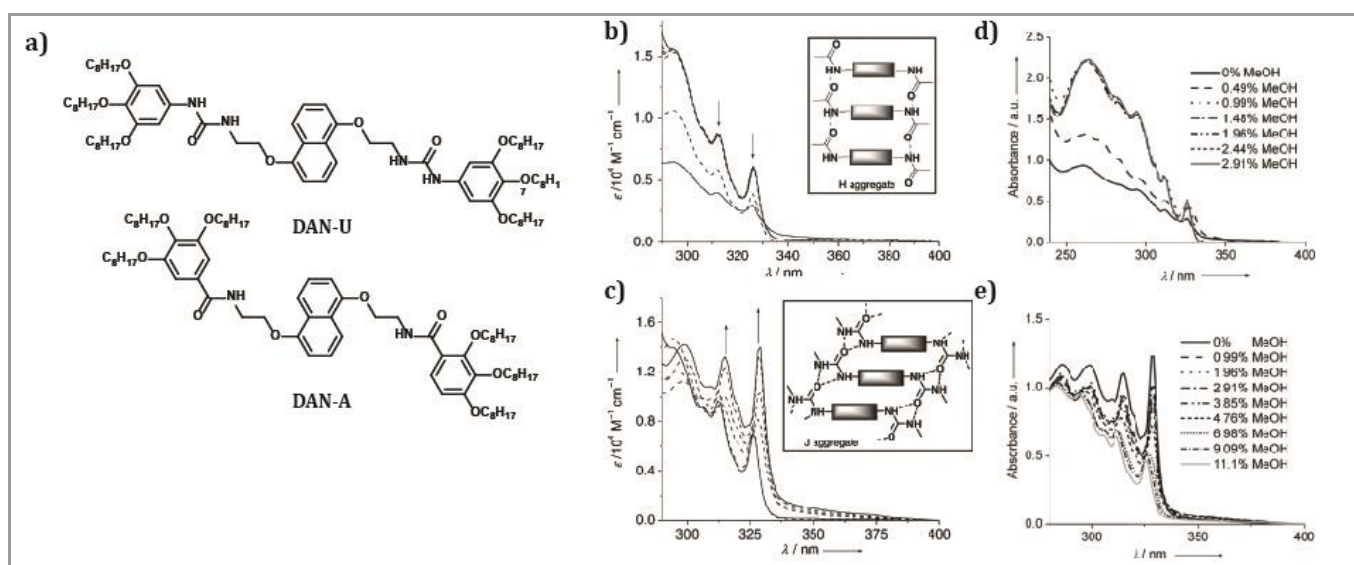
## 5. Urea-containing systems

Together with amides, urea groups are the most common H-bonding motifs that have been incorporated in multiple dyes to study their self-assembly properties. Das *et al.*[58] have studied the differences between amide and urea H-bonding motifs within the same  $\pi$ -conjugated system. They synthesized two derivatives of the dialkoxynaphthalene (DAN)  $\pi$ -system, namely, **DAN-U** and **DAN-A** (Figure 6a), which differ only in amide and urea functionalities. The authors observed that **DAN-U** formed J-aggregates in solution with a superior self-assembly propensity and thermal stability than the **DAN-A** system, which formed H-type aggregates. UV-Vis spectroscopy in solution showed the differences in aggregation at the same concentration and equal solvent (Figure 6b and 6c). To demonstrate the strength of the J-aggregates, absorption spectra were taken after the addition of progressive amounts of an H-bonding competing solvent (Figure 6d and 6e). The authors observed that for **DAN-U** the amount of methanol needed to disrupt the J-aggregate band and recover the monomeric state spectrum was larger (11%) than for **DAN-A** (less than 3%). The differences in self-assembly behavior also resulted in different gelation properties for the two systems. The urea-functionalized system showed gelation in a wide variety of organic solvents with higher thermal stability and lower critical gel concentration (CGC), whereas the amide-functionalized derivative formed gels with higher mechanical stability. These differences were explained by comparing the rigidity of the fibers formed by the gels. These findings are very relevant since they offer valuable information for the design of H-bonded semiconductors and the desired architectures they might form. Other urea-containing  $\pi$ -conjugated systems have been reported by Liu *et al.*[59] They reported a monopyrrolotetrathiafulvalene-based derivative containing a urea group and its gelation properties were explored. The urea TTF derivative was proven to be a non-gelator in single solvents, but it did gel mixtures of chloroform/dichloromethane and *n*-hexane. FT-IR spectroscopy, UV/Vis absorption spectroscopy, and SAXS (small angle X-ray scattering) revealed that in the organogel system, the gelators self-assembled into supramolecular networks with a J-type aggregation mode under the joint effect of  $\pi$ - $\pi$  stacking, intermolecular H-bonding, and van der Waals forces. The gel morphology obtained thanks to the J-aggregation mode of the TTF-urea derivative, provided the gel with great adsorption properties for other fluorescent dyes. Furthermore, the gel responded to external stimuli, making this assembly approach very appealing for the design of smart soft materials.

Urea H-bonding motifs have also been incorporated in bacteriochlorophylls (BChls) analogues, forming lamellar supramolecular structures exhibiting J-aggregation.[60] In the work of Shoji *et al.* there is a specific study on the effect of H-bonding in chlorosomal assemblies. Zinc BChl-d analogues with urea and amide H-bonding groups self-assembled in hexane solutions forming chlorosomal J-aggregates. The authors performed spectroscopic analysis of the BChls analogues and found that the formation of J-aggregates was assisted

additionally by H-bonding. The microscopy analysis showed the additional H-bonding units guided the assemblies into highly ordered supramolecular structures even compared to the tubular structures formed by BChl-d. The same group, has also reported artificial chlorosomal supramolecular nanosheets formed by the self-assembly of a zinc methoxy-chlorophyll derivative bearing amide and urea groups at the 17 position.[61] In this case, the zinc chlorophyll kinetically formed dimeric species that were transformed into thermodynamically more stable chlorosomal J-aggregates in the solid state. Once again, this was possible thanks to the additional H-bonding motifs pending from the main framework. The kinetic product had particle-like, while the thermodynamic product presented sheet-like nanostructures,

which is the first case of biomimetic supramolecular nanosheets of chlorosomal J-aggregates obtained from synthetic zinc chlorophyll derivatives with additional urea moieties. This molecular design offers several applications in artificial LH antennas and photosynthesis-inspired processes. Some of these studies also presented the ester-containing analogues as control molecules, not showing the same supramolecular structures and strongly coupled J-aggregates, highlighting the important role of having directional H-bonding groups.[60]



**Figure 6** a) Chemical structures of **DNA-U** and **DAN-A**. Solvent-dependent absorption spectra of **DAN-A** (b) and **DAN-U** (c): Arrows indicate direction of spectral changes from THF to MCH. Inset: schematic representation of the proposed mode of chromophore assembly (hydrogen bonding is shown with a dashed bond). Concentration of the chromophore = 0.1 mM and temperature = 25 °C. Effect of gradual addition of MeOH on the absorption spectra of the self-assembled structure of **DAN-A** (d) and **DAN-U** (e) in 95% MCH/THF. Concentration = 0.1 mM, Temperature = 25 °C. Reprinted with permission of (Das A, Ghosh S. Contrasting Self-Assembly and Gelation Properties among Bis-urea- and Bis-amide-Functionalised Dialkoxynaphthalene (DAN)  $\pi$  Systems. Chem – Eur J 2010; 16: 13622–13628). Copyright (2010).

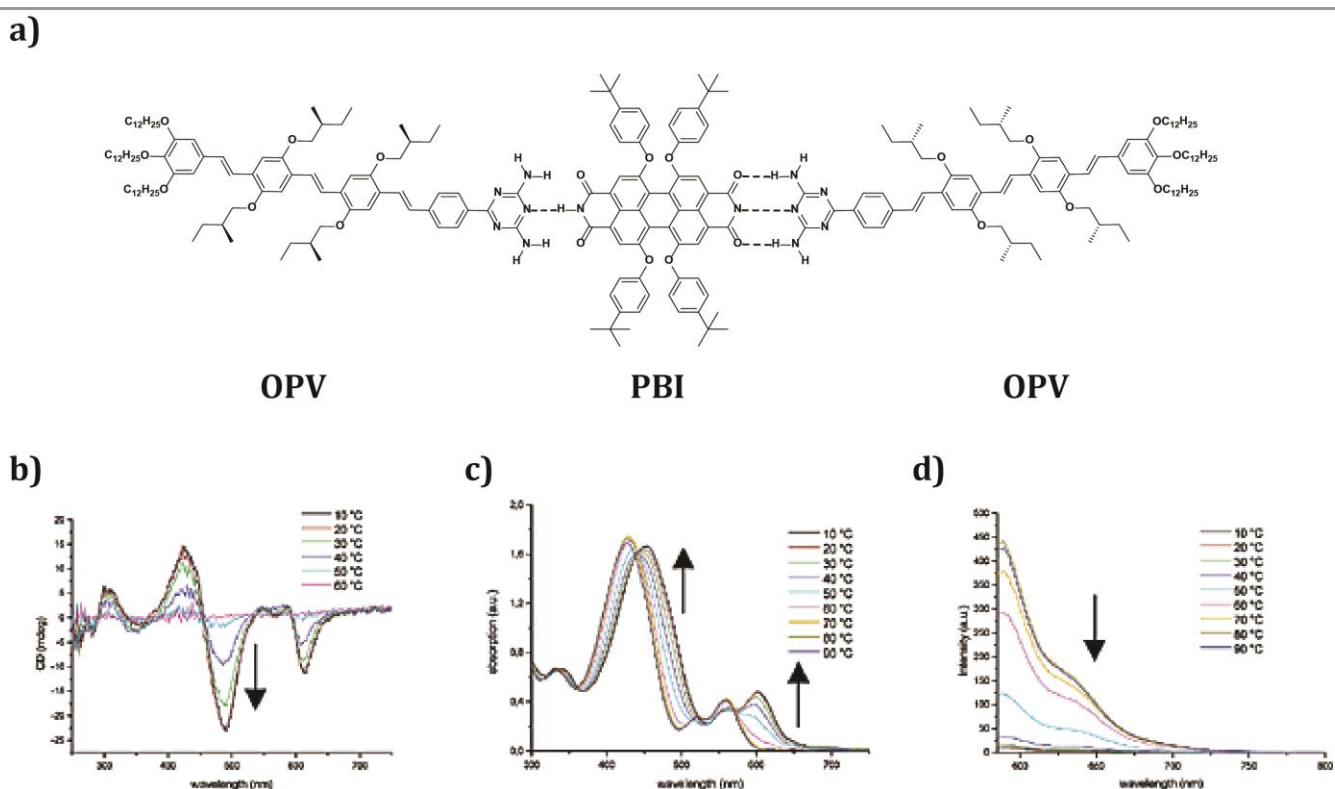
## 6. Systems containing complementary H-bonds

The arrangement of different  $\pi$ -conjugated components via complementary H-bonding is a great strategy towards highly organized structures with enhanced optoelectronic properties. Initial works by Schenning *et al.*[62] in 2002 show how  $\pi$ -conjugated systems with complementary H-bonding motifs result in photoinduced electron-transfer in donor-acceptor dyads (Figure 7a). The authors report the collective and hierarchical self-assembly of oligo(*p*-phenylene vinylene) (OPV) as the donor material and a **PBI** derivative as the acceptor, into chiral fibers. The **PBI** derivative has two complementary H-bonding binding sites for the diamino-triazine **OPV** (Figure 7a). The binding constant for this D-A-D system was low in chloroform, which is a good solvent, but it increased significantly in more apolar solvents, like MCH. The authors studied the self-assembly process of the D-A-D system doing UV/Vis, fluorescence and CD titration experiments. Regarding the absorption of the **PBI** component, a red-shift of  $\lambda_{\max}$  from 562 to 604 nm was observed, which is much larger than what is observed in **PBI** aggregates. The authors attribute such red-shift to the tight packing of dyes in a J-type aggregate. In this

case, there is fluorescence quenching, rationalized by electron transfer from the **OPV** component to the **PBI**. They observed that optimal quenching happened when all **PBI** binding sites are H-bonded to the **OPV** in a 1:2 ratio. Therefore, the authors suggested the H-bonded structure shown in figure 7a. Furthermore, a strong negative Cotton effect of the **PBI** was observed when adding progressively **OPV** chromophore, indicating the transfer of chirality of the OPV side chains to the **PBI** component. Similar results were found when the concentration of OPV was constant and **PBI** was added. With these optical activity results, the authors provided clear evidence that the D-A-D complex stacks into J-aggregates with a helical screw sense. Variable temperature spectroscopy was also carried out to complete the self-assembly study (Figure 7b, 7c and 7d). At high temperature (higher than 60 °C), the absorption spectra resemble the ones of the separate compounds in MCH at room temperature. Together with these changes in UV-Vis, the CD signal for both components is lower at temperature above 40 °C and completely disappeared at 60 °C. Upon cooling, the CD spectrum was fully recovered, indicating reversibility. Additionally, it was observed that the photoluminescence of the **PBI** increased at high temperature,

when the system is disassembled. The three techniques indicated the presence of aggregates at low temperature and molecularly dissolved monomeric species at high temperature, with a melting temperature of approximately 50 °C. Femtosecond pump-pulse spectroscopy measurements were performed in aggregated solutions to determine the charge transfer rate in the D-A-D system. When the D molecule is excited, the **OPV** radical cation becomes visible at 1450 nm, indicating a photoinduced electron-transfer process. At room temperature this charge-separated state is formed within a few

picoseconds, while the recombination is within 60 ps. At 80 °C where only monomers and small H-bonded complexes are present the charge formation is again within picoseconds, but the recombination is slower probably because after charge separation, the D-A-D complexes dissociate. With this work, the authors demonstrated that the organization of p-n heterojunctions was possible and that electronic processes can be controlled.



**Figure 7** a) Molecular structures of the **OPV** and **PBI** derivatives and their H-bonded assembly. Temperature-dependent CD (b), UV-vis (c), and fluorescence spectra (d) of the D-A-D triad (c). Concentration =  $3.7 \cdot 10^{-5}$  mol/L in MCH (arrows indicate the changes upon cooling). Reprinted with permission of (Schenning APHJ, v. Herrikhuizen J, Jonkheijm P, Chen Z, Würthner F, Meijer EW. Photoinduced Electron Transfer in Hydrogen-Bonded Oligo(p-phenylene vinylene)-Perylene Bisimide Chiral Assemblies. *J Am Chem Soc* 2002; 124: 10252–10253). Copyright (2002).

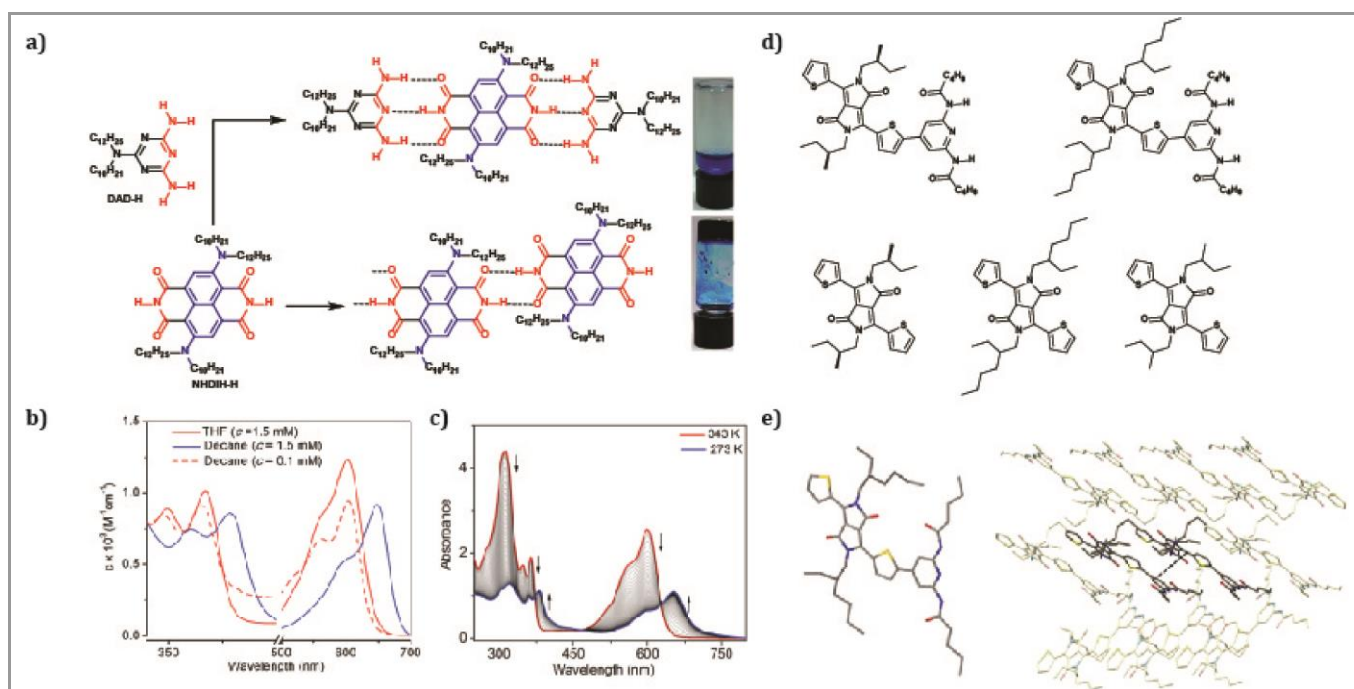
Other examples, like the work reported by Kar *et al.* [63] have shown a donor-acceptor-donor (D-A-D) core-substituted naphthalene-diimide (cNDI) chromophore, that exhibits highly cooperative J-aggregation leading to nanotubular assemblies and gelation in organic solvents. It was the first report of a H-bonding-initiated supramolecular polymerization of a diamino-substituted **cNDI** (NDI-H, Figure 8).[63] The authors showed that the tubular assembly enables very effective delocalization of excited states resulting in very long excited state lifetimes. They studied the supramolecular polymerization of **NDI-H** on a selection of organic solvents and they noted that in the presence of a D-A-D H-bonding competitor, gelation was prevented (Figure 8a). This was attributed to the **NDI-H** being endowed with a D-A-D type complementary H-bonding motif, indicating that supramolecular polymerization by extended H-bonded chain formation among the imide groups of the **NDI-H** is essential for gelation to occur. UV-Vis spectroscopy showed pronounced solvent effects, finding monomeric features in THF and a large bathochromic shift for the  $\pi-\pi^*$  band in n-decane, indicating J-aggregation. Additionally, the intramolecular

charge transfer band presented as well a bathochromic shift, indicating the reduction of the HOMO-LUMO gap due to effective delocalization of the charge transfer state in J-aggregates (Figure 8b). UV/Vis temperature-dependent studies were carried out in n-decane at different concentrations to further analyze the J-aggregate (Figure 8c). They observed that upon cooling, depletion of the absorption maxima at multiple wavelengths occurred at the expense of new red-shifted transitions, which were attributed to J-aggregation. The appearance of isosbestic points also revealed the thermodynamic equilibrium between monomeric and self-assembled species. When the fraction of aggregated species at different concentrations was plotted against temperature, sharp non-sigmoidal curves were obtained, thus indicating cooperative self-assembly. They proposed that **NDI-H** initially undergoes a linear oligomerization via H-bonding and when the length of the oligomer becomes sufficiently large, J-aggregation and alkyl chain packing become predominant, leading to the formation of a 2D sheet that eventually bends to generate nanotubes. They concluded that J-aggregated dye

molecules encapsulated in the multilayer walls of the tubes, facilitate very effective delocalization of the excited states, yielding remarkably prolonged excited state lifetimes.

Braunschweig *et al.* have recently studied how the conjugation length, solubilizing side chains and the type of H-bonding groups affect the homo-assembly of **DPPs** into J-aggregates.[23] These measurements were performed through temperature dependent UV/Vis titrations in toluene on multiple thiophene **DPP** derivatives (Figure 8d and 8e). They found out that the presence of diamidopyridine (DAP) groups, known for their H-bonding ability, improved considerably the driving force for assembly into larger clusters compared to those without the **DAP** group. These findings described the intricate contributions between H-bonding,  $\pi$ - $\pi$  stacking, van der Waals forces, solvent, concentration and temperature that

is responsible for the size, structure, stability and spectroscopic attributes of the resulting superstructures. Furthermore, their main finding was that these molecules assemble into J-aggregates, since they obtained crystalline structures where the molecules appeared in slip-stack geometries (Figure 8e). The authors derived two equations for the calculation of the size of an aggregated stack and its average mole fraction. These discoveries are very relevant, since the structure and properties of supramolecular assemblies are intimately linked, impacting the design of devices. Furthermore, the authors have explored complementary H-bonded **DPPs** and **PBIs/NDIs** systems, finding interesting effects on the excited-state dynamics and on the activation of new pathways, such as singlet fission.[65]



**Figure 8** a) H-bond driven supramolecular polymerization and gelation (right, bottom) of **NDI-H** in *n*-decane ( $c = 4.0$  mM). The addition of a **DAD** H-bonding competitor (2.0 equiv.), prevents the gelation (right, top). b) Solvent- and concentration-dependent UV/Vis spectra (intensity normalized with concentration) of **NDI-H** ( $l = 0.1$  cm,  $T = 298$  K). c) Temperature-dependent UV/Vis experiments of **NDI-H** (1.75 mM, decane). Arrows indicate the spectral changes upon decreasing the temperature. d) Molecular structures of the **DPP** derivatives studied. e) Single crystal structure of the **DPP** derivative modified with diamidopyridine. Reprinted with permissions of (Kar H, W. Gehrig D, Kumar Allampally N, Fernández G, Laqui F, Ghosh S. Cooperative supramolecular polymerization of an amine-substituted naphthalene-diimide and its impact on excited state photophysical properties. *Chem Sci* 2016; 7: 1115–1120). Copyright (2016) and (Zhou Y, Guzman CX, Helguero-Kelley LC, Liu C, Peurifoy SR, Captain B, Braunschweig AB. Diketopyrrolopyrrole assembly into J-aggregates. *J Phys Org Chem* 2016; 29: 689–699). Copyright (2016).

## 7. Systems with other H-bonding functionalities

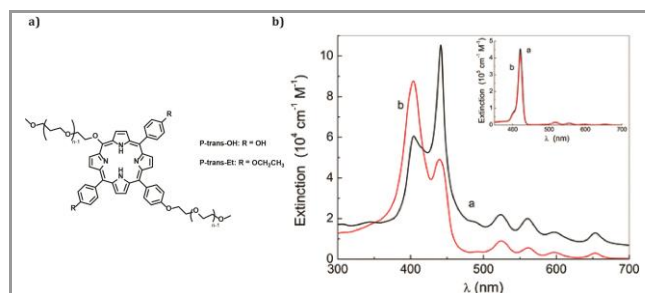
Examples of molecules containing hydroxyl functional groups and displaying J-aggregate formation have also been reported. For instance, Micali *et al.*[66] have compared two porphyrin derivatives (**P-trans-OH** and **P-trans-Et**). **P-trans-OH** contains free hydroxyl groups at the periphery, while **P-trans-E** has etoxy groups (Figure 9a). Both derivatives form large aggregates, but **P-trans-OH** forms J-type aggregates, as evidenced by the red-shifted main extinction band (Figure 9b) and a shortening of the fluorescence lifetime. On the other hand, the substitution of  $-\text{OH}$  by  $-\text{OCH}_2\text{CH}_3$  results in the formation of H-type aggregates, which appeared as a blue-shifted transition in the UV-Vis spectrum and the long fluorescence lifetime. The results obtained with different spectroscopy techniques showed that H-bonding guides the

assemblies to form J-aggregates. The measurements were performed in aqueous solutions, achieving aggregation through H-bonding and avoiding competition with the water molecules. This result is important to design systems that mimic natural systems and that can be applied in bioelectronic devices.

Our group has recently shown H-bonded thiophene-capped **DPP** derivatives functionalized with semicarbazone groups displaying J-aggregates[67] that had different intensities depending on the solvent used. While chloroform solutions did not show any types of aggregates, chlorobenzene and toluene solutions showed an additional red-shifted band that increased dramatically in ethyl acetate. FTIR (Fourier transform) spectroscopy in solution showed the formation of H-bonds and we confirmed that the J-aggregates were formed by H-bonding interactions by adding an H-bonding competing solvent (methanol). The J-aggregate band totally disappeared after the

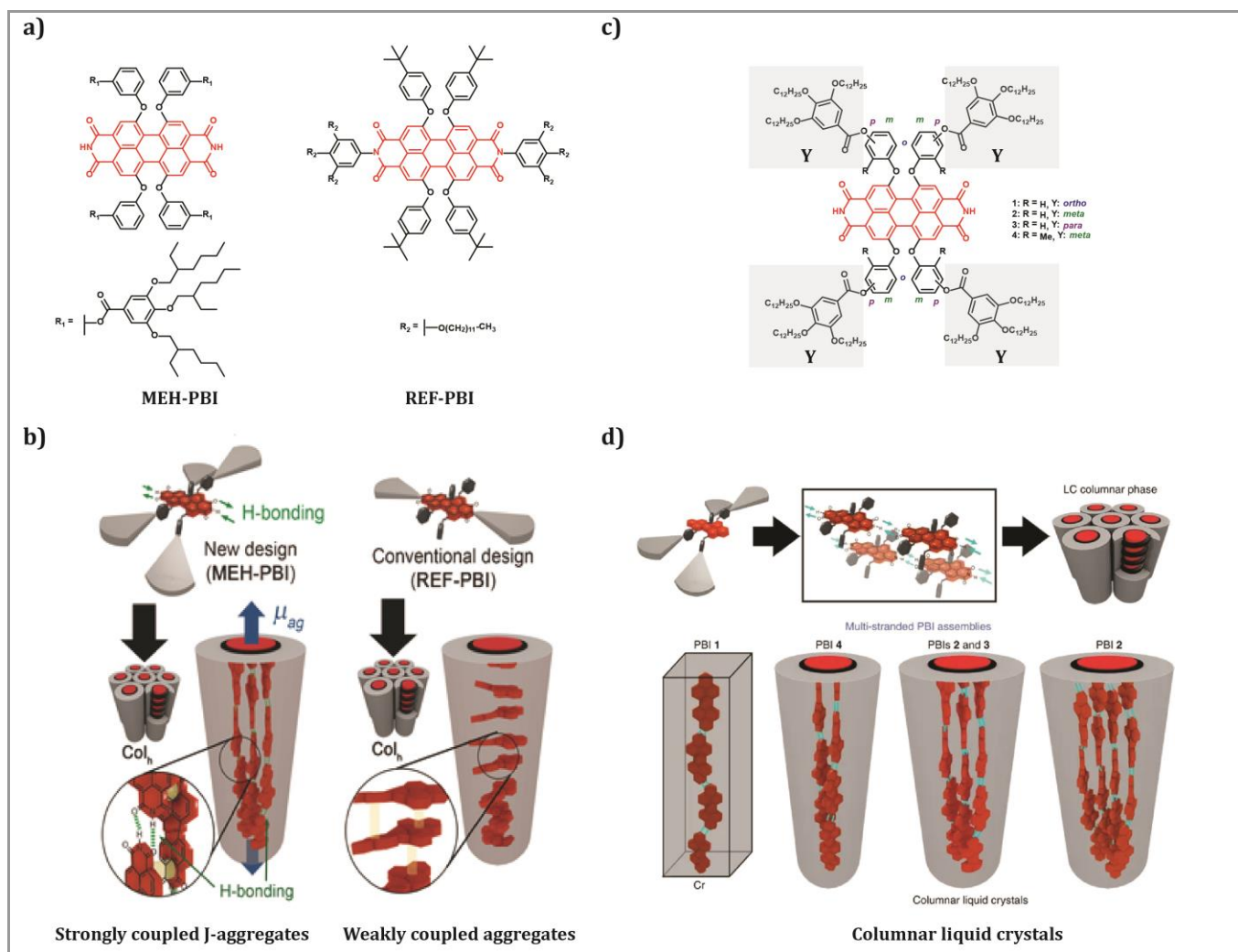
addition of specific amounts of methanol. J-aggregates were also present in solutions of self-assembly promoting solvents at room temperature and they shaded upon increasing the temperature. Nevertheless, J-aggregates were still observed at high temperatures (up to 60 °C), highlighting the strength of the assemblies. With this strategy, it was possible to tune the optoelectronic properties, such as the optical energy band gap or the coverage of the solar spectrum through aggregation.

**PBIs** using the imide groups to form H-bonds have been extensively studied.[42] In 2017 Würthner *et al.* reported the achievement of an unprecedented organization of **PBI** in a columnar liquid-crystalline (LC) phase, for which the transition dipole moments of the dye were oriented parallel to the columnar axes (Figure 10).[68] This dye holds 2-ethylhexyl-substituted gallic acid residues at the *meta*-positions in a tetraphenoxy-functionalized perylene bisimide (MEH-PBI) possessing N—H groups at the imide positions (Figure 10a) that self-assembles forming J-aggregates through H-bonds and  $\pi$ — $\pi$  interactions.



**Figure 9** a) Molecular structures of **P-trans-OH** and **P-trans-Et**. b) Extinction spectra of **P-trans-OH** (curve a) and **P-trans-Et** (curve b) in water. The inset shows the corresponding absorption spectra in THF. Reprinted with the permission of (Villari V, Mineo P, Scamporrino E, Micali N. Role of the hydrogen-bond in porphyrin J-aggregates. RSC Adv 2012; 2: 12989–12998). Copyright (2012).

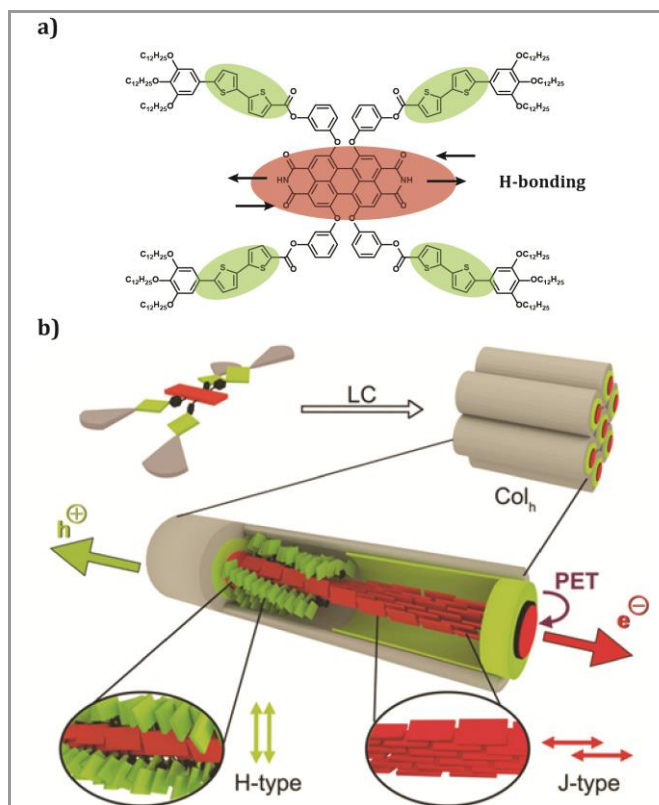
Usually, **PBI** liquid crystals are prepared by functionalizing the **PBI** core with mesogenic units at the imide positions, leading to the spontaneous stacking of the **PBI** cores through co-facial  $\pi$ — $\pi$  interactions forming columnar assemblies. This type of assembly was also reported for **REF-PBI** (Figure 10a and 10b), leading to aggregates with a broad and slightly red-shifted



**Figure 10** a) Molecular structures of **MEH-PBI** and reference molecule **REF-PBI**. b) Illustration of the molecular self-assembly of **MEH-PBI** and **REF-PBI** into columnar hexagonal LC phases that exhibit orthogonal orientation of the **PBIs**. Blue arrows indicate the direction of the main transition dipole moments ( $\mu_{ag}$ ) of the **PBI** molecules for **MEH-PBI**. Reprinted with permission from (S. Herbst, B. Soberats, P. Leowanawat, M. Lehmann, F. Würthner, *Angew. Chem. Int. Ed.* **2017**, *56*, 2162–2165. Copyright (2017). John Wiley and Sons). c) Chemical structures of **PBIs 1–4**. d) Schematic illustration of the different columnar assemblies composed of one, two, three, and four strands. The helicity in the columnar assemblies of **PBIs 2–4** has been chosen to be (P) for graphical representation. Please note that **PBIs 1–4** are racemic and therefore (P) and (M) helices may coexist in the corresponding columnar phases.

absorption band and a LC columnar hexagonal phase. However, by bay tetrasubstituting **PBIs** with free NH groups at the imide positions, strongly coupled J-aggregates were obtained (Figure 10b). These J-aggregates were formed upon self-assembly in methylcyclohexane (MCH), which directed the formation of 1D helical structures with exciton migration over distances up to 100 nm.[35] Through a series of spectroscopy analysis and model simulations, they confirmed this unprecedented self-assembly arrangement for columnar LCs and established that its transition dipole moment is oriented parallel to the columnar axis; whereas for **REF-PBI** (as for other common discotic LCs), the orientation of the transition dipole moment is orthogonal to the column axis. These molecules are strongly coupled in 1D J-aggregates and can be aligned in anisotropic thin films, opening up new perspectives in the field of photonic materials. In a more recent work, Herbst *et al.*[69] continued studying the assembly mode for columnar **PBI** LCs analyzing the driving forces participating in the assembly process, and understanding how to control the number of strands in the columns via molecular engineering of the **PBI** building blocks. In this work, they reported how the molecular engineering of tetra-bay dendronized **PBIs** (**PBIs 1–4**, Figure 10c) can serve in the design of complex supramolecular assemblies packing patterns, along with interesting optical properties. They described the self-assembly behavior of the **PBI** dyes self-organizing into one-, two-, three-, or four- stranded J-aggregates within crystalline and columnar LC phases (Figure 10d). They were able to tune the composition of these columnar assemblies through the molecular design guided by the corresponding dendron wedges; determining that the relative position of the dendrons at the phenoxy spacers of the **PBI** cores is the key factor that governs the respective packing structure via steric requirements, influencing parameters such as the helical pitch, the twist of the perylenes and the number of strands in a single column. The authors used a wide variety of spectroscopic techniques and theoretical models to analyze all the structural features of these columnar LCs. Spectroscopic investigations were made since the different organizations of **PBIs 1–4** offer the opportunity for elucidating the influence of particular packing arrangements on functional properties of dye aggregates, especially in terms of exciton coupling. By comparing the optical properties in the bulk state to the ones of their monomers in solution through UV-vis absorption spectra, a slight bathochromic shift with retained vibronic structure was observed for **PBI 1**, which supports that this compound does not pack in multiple strands due to the steric effects imparted by the *ortho*-substitution. In contrast, the other **PBIs** showed pronounced bathochromic shifts of  $\lambda_{\text{max}}$ , which was strongest for double-stranded **PBI 4** ( $>2000\text{ cm}^{-1}$ ) and decreased with increasing number of strands from **PBI 3** ( $>1800\text{ cm}^{-1}$ ; three strands) to the quadruple-stranded **PBI 2** ( $>1700\text{ cm}^{-1}$ ). All these structural features directly convert into functional properties due to the electronic coupling of the transition dipole moments of the closely stacked dyes. Thus, demonstrating that the bathochromic shift of the absorption maximum in the aggregated state relative to the monomer depends on the number of self-assembled strands and yields the best J-aggregate for the double-stranded arrangement of **PBI 4**, meaning that strongly coupled J-aggregates are promising materials for photonic applications.

More recently Hecht *et al.* have synthesized a novel core-shell structured columnar LC, composed of a D-A dyad of tetraphenoxy **PBI** containing four bithiophene units at the periphery, **PBI 2T** (Figure 11a).[70] This molecule self-assembles in solution into helical J-aggregates guided by  $\pi$ - $\pi$  interactions and H-bonds (Figure 11b), which organizes into LC columnar hexagonal domain in the solid state. The properties of **PBI 2T** were studied by UV/Vis absorption and fluorescence spectroscopy, focusing on photoinduced electron-transfer (PET) and energy-transfer (ET). An optical signature of monomerically dissolved tetraphenoxy-substituted **PBIs** was observed from the UV/Vis absorption spectrum of **PBI 2T** in chloroform, with a prominent  $S_0$ — $S_1$  transition at 569 nm. An additional strong absorption band can be seen at 385 nm, corresponding to the four electron-rich bithiophene side arms. Furthermore, these UV/Vis absorption spectra also unveiled the contrasting coupling behavior of the two chromophores within **PBI 2T**. A model of the helical structure of **PBI 2T** was generated based on the experimental data. The **PBIs** were modeled to form a H-bonded sextuple-stranded helix with slipped-stack arranged chromophores. Theoretically, this sextuple-stranded self-assembly mode should enable highly efficient exciton transport over long distances, as similar **PBI** J-aggregates with smaller number of strands, which have shown long exciton lifetimes, allowing exciton transport over distances of roughly 70 nm.[35] The authors hypothesized that a higher number of strands in the core-shell structure of **PBI 2T** should improve its capability to avoid trap-sites within the aggregate, therefore improving exciton mobility. This suggested that the material could be suitable for photoconducting applications and for this purpose, devices were fabricated by spin-casting a solution of **PBI 2T** onto bottom contact Si/SiO<sub>2</sub> substrates with grid-like gold electrodes. The active layer in these devices showed a linear response to light intensity, with instant switching times within the measuring interval of the experiment. The benefits of the A-D core-shell architecture were notoriously evident when they compared these values to the ones obtained from devices that were fabricated with the parent compound from which **PBI 2T** was derived, which exhibited a quadruple-stranded  $14_1$  helix in the LC state. The interaction between PET and charge transport along the self-assembled core-shell structure, allowed the implementation of the dye in two-contact photoconductivity devices, giving rise to a 20-fold increased photoresponse compared to a reference dye without bithiophene donor moieties.[69]



**Figure 11** a) Chemical structure of PBI 2T. b) Illustration of the molecular arrangement of PBI 2T in the columnar hexagonal LC phase with J-coupled PBIs (red) and H-coupled bithiophene units (green). The purple arrow indicates the photoinduced electron transfer (PET) and the consecutive electron and hole transport along the columnar core-shell structure. The helicity in the shown columnar assembly has been chosen to be (P) for graphical representation. Please note that PBI 2T is achiral and therefore (P) and (M) helices may coexist in the LC phase. Reprinted with permission of (Hecht M, Schlossarek T, Stolte M, Lehmann M, Würthner F. Photoconductive Core-Shell Liquid-Crystals of a Perylene Bisimide J-Aggregate Donor-Acceptor Dyad. *Angew Chem Int Ed* 2019; 58: 12979–12983). Copyright (2019).

## 8. Conclusions

We have provided an overview on the most relevant and recent examples in the field of H-bonded  $\pi$ -conjugated systems showing J-type aggregation. The additional H-bonding moieties incorporated into the chemical structures of chromophores result in slipped-stack aggregates with strong exciton coupling. Such arrangement has been proven to be very beneficial for charge transport, making this supramolecular strategy very attractive in the field of organic electronics. Several hydrogen-bonding units have been discussed, offering chemical design tools to achieve supramolecular structures where excitons can be transported over a large amount of  $\pi$ -conjugated cores. Furthermore, the versatility of this approach, that includes multiple dyes and H-bonding functionalities, can help in the continuous search for novel materials in light harvesting systems, electronics and photonics.

## Funding Information

LabEx Emerging Investigators Grant 2018 from the Fondation pour la Recherche en Chimie.

## Acknowledgment

The authors thank the Foundation for Frontier Research in Chemistry (FRC) LabEx Emerging Investigators Grant 2018 and CNRS for financial support. We kindly thank Dr. Philippe Mésini for fruitful discussion.

## References

- Lehn J-M. *Supramolecular Chemistry—Scope and Perspectives Molecules, Supermolecules, and Molecular Devices* (Nobel Lecture). *Angew Chem Int Ed Engl* 1988; 27: 89–112
- Lehn J-M. *Towards Complex Matter: Supramolecular Chemistry and Self-organization\**. *Eur Rev* 2009; 17: 263–280
- Lehn J-M. *Perspectives in Supramolecular Chemistry—From Molecular Recognition towards Molecular Information Processing and Self-Organization*. *Angew Chem Int Ed Engl* 1990; 29: 1304–1319
- Fyfe MCT, Stoddart JF. *Synthetic Supramolecular Chemistry*. *Acc Chem Res* 1997; 30: 393–401
- Stupp SI, Palmer LC. *Supramolecular Chemistry and Self-Assembly in Organic Materials Design*. *Chem Mater* 2014; 26: 507–518
- González-Rodríguez D, Schenning APHJ. *Hydrogen-bonded Supramolecular  $\pi$ -Functional Materials* †. *Chem Mater* 2011; 23: 310–325
- Steiner T. *The Hydrogen Bond in the Solid State*. *Angew Chem Int Ed* 2002; 41: 48–76
- Prins LJ, Reinhoudt DN, Timmerman P. *Noncovalent Synthesis Using Hydrogen Bonding*. *Angew Chem Int Ed* 2001; 40: 2382–2426
- Ruiz-Carretero A, Ravelo NRÁ, Militzer S, Mésini PJ. *Hydrogen-bonded diketopyrrolopyrrole derivatives for energy-related applications*. *J Mater Chem A* 2019; 7: 23451–23475
- Schoonbeek FS, Esch JH van, Wegewijs B, Rep DBA, Haas MP de, Klapwijk TM, Kellogg RM, Feringa BL. *Efficient Intermolecular Charge Transport in Self-Assembled Fibers of Mono- and Bithiophene Bisurea Compounds*. *Angew Chem Int Ed* 1999; 38: 1393–1397
- Gospodinova N, Tomšík E. *Hydrogen-bonding versus  $\pi$ - $\pi$  stacking in the design of organic semiconductors: From dyes to oligomers*. *Prog Polym Sci* 2015; 43: 33–47
- Jelley EE. *Molecular, Nematic and Crystal States of I: I-Diethyl-Cyanine Chloride*. *Nature* 1937; 139: 631–631
- Scheibe G. *Über die Veränderlichkeit der Absorptionsspektren in Lösungen und die Nebenvalenzen als ihre Ursache*. *Angew Chem* 1937; 50: 212–219
- Bücher H, Kuhn H. *Scheibe aggregate formation of cyanine dyes in monolayers*. *Chem Phys Lett* 1970; 6: 183–185

- 
- <sup>15</sup>Hestand NJ, Spano FC. Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer. *Chem Rev* 2018; Im Internet: <https://doi.org/10.1021/acs.chemrev.7b00581>
- <sup>16</sup>Tani T. Review of mechanisms of photographic sensitivity. *Imaging Sci J* 2007; 55: 65–79
- <sup>17</sup>Takeyuki Kawaguchi, Kaoru Iwata. Merocyanine J aggregates: Formation and structural change on chemical and thermal treatments. *Thin Solid Films* 1990; 191: 173–191
- <sup>18</sup>Paternò GM, Moretti L, Barker AJ, D'Andrea C, Luzio A, Barbero N, Galliano S, Barolo C, Lanzani G, Scotognella F. Near-infrared emitting single squaraine dye aggregates with large Stokes shifts. *J Mater Chem C* 2017; 5: 7732–7738
- <sup>19</sup>Kaiser TE, Stepanenko V, Würthner F. Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure–Property Relationship, Nucleation–Elongation Mechanism, and Sergeants-and-Soldiers Principle. *J Am Chem Soc* 2009; 131: 6719–6732
- <sup>20</sup>Würthner F, Thalacker C, Diele S, Tschierske C. Fluorescent J-type Aggregates and Thermotropic Columnar Mesophases of Perylene Bisimide Dyes. *Chem – Eur J* 2001; 7: 2245–2253
- <sup>21</sup>Crusats J, El-Hachemi Z, Escudero C, Ribó JM. Case history of porphyrin J-aggregates: a personal point of view. *J Porphyr Phthalocyanines* 2009; 13: 461–470
- <sup>22</sup>Song Q, Jiao Y, Wang Z, Zhang X. Tuning the Energy Gap by Supramolecular Approaches: Towards Near-Infrared Organic Assemblies and Materials. *Small* 2016; 12: 24–31
- <sup>23</sup>Zhou Y, Guzman CX, Helguero-Kelley LC, Liu C, Peurifoy SR, Captain B, Braunschweig AB. Diketopyrrolopyrrole assembly into J-aggregates. *J Phys Org Chem* 2016; 29: 689–699
- <sup>24</sup>Sengupta S, Würthner F. Chlorophyll J-Aggregates: From Bioinspired Dye Stacks to Nanotubes, Liquid Crystals, and Biosupramolecular Electronics. *Acc Chem Res* 2013; 46: 2498–2512
- <sup>25</sup>Balaban TS, Tamiaki H, Holzwarth AR. Chlorins Programmed for Self-Assembly. In: Würthner F (Hrsg.). *Supramolecular Dye Chemistry*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2005: 1–38 Im Internet: <https://doi.org/10.1007/b137480>
- <sup>26</sup>Egawa Y, Hayashida R, Anzai J. pH-Induced Interconversion between J-Aggregates and H-Aggregates of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin in Polyelectrolyte Multilayer Films. *Langmuir* 2007; 23: 13146–13150
- <sup>27</sup>Würthner F, Kaiser TE, Saha-Möller CR. J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials. *Angew Chem Int Ed* 2011; 50: 3376–3410
- <sup>28</sup>Spano FC. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Acc Chem Res* 2010; 43: 429–439
- <sup>29</sup>Fidder H, Terpstra J, Wiersma DA. Dynamics of Frenkel excitons in disordered molecular aggregates. *J Chem Phys* 1991; 94: 6895–6907
- <sup>30</sup>Ghosh PN. Davydov splitting and multipole interactions. *Solid State Commun* 1976; 19: 639–642
- <sup>31</sup>Scheblykin IG, Bataiev MM, Van der Auweraer M, Vitukhnovsky AG. Dimensionality and temperature dependence of the radiative lifetime of J-aggregates with Davydov splitting of the exciton band. *Chem Phys Lett* 2000; 316: 37–44
- <sup>32</sup>Scheblykin IG, Sliusarenko OY, Lepnev LS, Vitukhnovsky AG, Van der Auweraer M. Excitons in Molecular Aggregates of 3,3'-Bis-[3-sulfopropyl]-5,5'-dichloro-9-ethylthiacarbocyanine (THIATS): Temperature Dependent Properties. *J Phys Chem B* 2001; 105: 4636–4646
- <sup>33</sup>Dahlbom M, Pullerits T, Mukamel S, Sundström V. Exciton Delocalization in the B850 Light-Harvesting Complex: Comparison of Different Measures. *J Phys Chem B* 2001; 105: 5515–5524
- <sup>34</sup>Kühn O, Sundström V, Pullerits T. Fluorescence depolarization dynamics in the B850 complex of purple bacteria. *Chem Phys* 2002; 275: 15–30
- <sup>35</sup>Lin H, Camacho R, Tian Y, Kaiser TE, Würthner F, Scheblykin IG. Collective Fluorescence Blinking in Linear J-Aggregates Assisted by Long-Distance Exciton Migration. *Nano Lett* 2010; 10: 620–626
- <sup>36</sup>Hydrogen bonding ability of the amide group. Im Internet: <https://pubs.acs.org/doi/pdf/10.1021/ja00819a013>
- <sup>37</sup>Tsai W-W, Tevis ID, Tayi AS, Cui H, Stupp SI. Semiconducting Nanowires from Hairpin-Shaped Self-Assembling Sexithiophenes †. *J Phys Chem B* 2010; 114: 14778–14786
- <sup>38</sup>Tevis ID, Tsai W-W, Palmer LC, Aytun T, Stupp SI. Grooved Nanowires from Self-Assembling Hairpin Molecules for Solar Cells. *ACS Nano* 2012; 6: 2032–2040
- <sup>39</sup>Ghosh S, Cherumukkil S, Suresh CH, Ajayaghosh A. A Supramolecular Nanocomposite as a Near-Infrared-Transmitting Optical Filter for Security and Forensic Applications. *Adv Mater* 2017; 29: 1703783
- <sup>40</sup>Ghosh S, Das S, Saeki A, Praveen VK, Seki S, Ajayaghosh A. A Hybrid Organogel of a Low Band Gap Diketopyrrolopyrrole with PC<sub>71</sub>BM: Phase Separated Morphology and Enhanced Photoconductivity. *ChemNanoMat* 2018; 4: 831–836
- <sup>41</sup>Kaneko R, Chowdhury TH, Sugawa K, Lee J-J, Otsuki J, Islam A. Electro-active nanofibers of a tetrathiafulvalene derivative
-

- 
- with amide hydrogen bonds as a dopant-free hole transport material for perovskite solar cells. *Sol Energy* 2019; 194: 248–253
- <sup>42</sup> Würthner F. Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures. *Chem Commun* 2004; 1564–1579
- <sup>43</sup> Ghosh S, Li X-Q, Stepanenko V, Würthner F. Control of H- and J-Type  $\pi$  Stacking by Peripheral Alkyl Chains and Self-Sorting Phenomena in Perylene Bisimide Homo- and Heteroaggregates. *Chem – Eur J* 2008; 14: 11343–11357
- <sup>44</sup> Wagner W, Wehner M, Stepanenko V, Ogi S, Würthner F. Living Supramolecular Polymerization of a Perylene Bisimide Dye into Fluorescent J-Aggregates. *Angew Chem* 2017; 129: 16224–16228
- <sup>45</sup> Ogi S, Stepanenko V, Sugiyasu K, Takeuchi M, Würthner F. Mechanism of Self-Assembly Process and Seeded Supramolecular Polymerization of Perylene Bisimide Organogelator. *J Am Chem Soc* 2015; 137: 3300–3307
- <sup>46</sup> Ogi S, Stepanenko V, Thein J, Würthner F. Impact of Alkyl Spacer Length on Aggregation Pathways in Kinetically Controlled Supramolecular Polymerization. *J Am Chem Soc* 2016; 138: 670–678
- <sup>47</sup> Ogi S, Fukaya N, Arifin, Skjelstad BB, Hijikata Y, Yamaguchi S. Seeded Polymerization of an Amide-Functionalized Diketopyrrolopyrrole Dye in Aqueous Media. *Chem – Eur J* 2019; 25: 7303–7307
- <sup>48</sup> Zou Q, Liu K, Abbas M, Yan X. Peptide-Modulated Self-Assembly of Chromophores toward Biomimetic Light-Harvesting Nanoarchitectonics. *Adv Mater* 2016; 28: 1031–1043
- <sup>49</sup> Smith KH, Tejada-Montes E, Poch M, Mata A. Integrating top-down and self-assembly in the fabrication of peptide and protein-based biomedical materials. *Chem Soc Rev* 2011; 40: 4563–4577
- <sup>50</sup> Sun Y, Jiang L, Schuermann KC, Adriaens W, Zhang L, Boey FYC, De Cola L, Brunsveld L, Chen X. Semiconductive, One-Dimensional, Self-Assembled Nanostructures Based on Oligopeptides with  $\pi$ -Conjugated Segments. *Chem - Eur J* 2011; 17: 4746–4749
- <sup>51</sup> Kumar RJ, MacDonald JM, Singh TB, Waddington LJ, Holmes AB. Hierarchical Self-Assembly of Semiconductor Functionalized Peptide  $\alpha$ -Helices and Optoelectronic Properties. *J Am Chem Soc* 2011; 133: 8564–8573
- <sup>52</sup> Jintoku H, Sagawa T, Miyamoto K, Takafuji M, Ihara H. Highly efficient and switchable electron-transfer system realised by peptide-assisted J-type assembly of porphyrin. *Chem Commun* 2010; 46: 7208–7210
- <sup>53</sup> Koti ASR, Periasamy N. Self-Assembly of Template-Directed J-Aggregates of Porphyrin. *Chem Mater* 2003; 15: 369–371
- <sup>54</sup> Kim JH, Lee M, Lee JS, Park CB. Self-Assembled Light-Harvesting Peptide Nanotubes for Mimicking Natural Photosynthesis. *Angew Chem Int Ed* 2012; 51: 517–520
- <sup>55</sup> Xue B, Li Y, Yang F, Zhang C, Qin M, Cao Y, Wang W. An integrated artificial photosynthesis system based on peptide nanotubes. *Nanoscale* 2014; 6: 7832–7837
- <sup>56</sup> Kim JH, Nam DH, Lee YW, Nam YS, Park CB. Self-Assembly of Metalloporphyrins into Light-Harvesting Peptide Nanofiber Hydrogels for Solar Water Oxidation. *Small* 2014; 10: 1272–1277
- <sup>57</sup> Smith AM, Williams RJ, Tang C, Coppo P, Collins RF, Turner ML, Saiani A, Ulijn RV. Fmoc-Diphenylalanine Self Assembles to a Hydrogel via a Novel Architecture Based on  $\pi$ - $\pi$  Interlocked  $\beta$ -Sheets. *Adv Mater* 2008; 20: 37–41
- <sup>58</sup> Das A, Ghosh S. Contrasting Self-Assembly and Gelation Properties among Bis-urea- and Bis-amide-Functionalised Dialkoxynaphthalene (DAN)  $\pi$  Systems. *Chem – Eur J* 2010; 16: 13622–13628
- <sup>59</sup> Liu Y, Liu L, Zhu E, Yue M, Gao C, Wu X, Che G, Liu H. Gel Formed by Self-Assembly of a Urea-Modified Monopyrrolotetrafulvalene Derivative Displays Multi-Stimuli Responsiveness and Absorption of Rhodamine B. *ChemPlusChem* 2018; 83: 1109–1118
- <sup>60</sup> Shoji S, Ogawa T, Hashishin T, Tamiaki H. Self-Assemblies of Zinc Bacteriochlorophyll-d Analogues Having Amide, Ester, and Urea Groups as Substituents at 17-Position and Observation of Lamellar Supramolecular Nanostructures. *ChemPhysChem* 2018; 19: 913–920
- <sup>61</sup> Shoji S, Ogawa T, Matsubara S, Tamiaki H. Bioinspired supramolecular nanosheets of zinc chlorophyll assemblies. *Sci Rep* 2019; 9: 1–8
- <sup>62</sup> Schenning APHJ, v. Herrikhuyzen J, Jonkheijm P, Chen Z, Würthner F, Meijer EW. Photoinduced Electron Transfer in Hydrogen-Bonded Oligo(p-phenylene vinylene)-Perylene Bisimide Chiral Assemblies. *J Am Chem Soc* 2002; 124: 10252–10253
- <sup>63</sup> Kar H, W. Gehrig D, Kumar Allampally N, Fernández G, Laquai F, Ghosh S. Cooperative supramolecular polymerization of an amine-substituted naphthalene-diimide and its impact on excited state photophysical properties. *Chem Sci* 2016; 7: 1115–1120
- <sup>64</sup> Zhou Y, Guzman CX, Helguero-Kelley LC, Liu C, Peurifoy SR, Captain B, Braunschweig AB. Diketopyrrolopyrrole assembly into J-aggregates: Diketopyrrolopyrrole Assembly into J-aggregates. *J Phys Org Chem* 2016; 29: 689–699
-

<sup>65</sup> Levine AM, Schierl C, Basel BS, Ahmed M, Camargo BA, Guldi DM, Braunschweig AB. Singlet Fission in Combinatorial Diketopyrrolopyrrole-Rylene Supramolecular Films. *J Phys Chem C* 2019; 123: 1587–1595

<sup>66</sup> Villari V, Mineo P, Scamporrino E, Micali N. Role of the hydrogen-bond in porphyrin J-aggregates. *RSC Adv* 2012; 2: 12989–12998

<sup>67</sup> Militzer S, Tran TMP, Mésini PJ, Ruiz-Carretero A. Tuning the Optical and Self-Assembly Properties of Diketopyrrolopyrrole Semicarbazone Derivatives through Hydrogen Bonding. *ChemNanoMat* 2018; 4: 790–795

<sup>68</sup> Herbst S, Soberats B, Leowanawat P, Lehmann M, Würthner F. A Columnar Liquid-Crystal Phase Formed by Hydrogen-

Bonded Perylene Bisimide J-Aggregates. *Angew Chem Int Ed* 2017; 56: 2162–2165

<sup>69</sup> Herbst S, Soberats B, Leowanawat P, Stolte M, Lehmann M, Würthner F. Self-assembly of multi-stranded perylene dye J-aggregates in columnar liquid-crystalline phases. *Nat Commun* 2018; 9: 1–9

<sup>70</sup> Hecht M, Schlossarek T, Stolte M, Lehmann M, Würthner F. Photoconductive Core-Shell Liquid-Crystals of a Perylene Bisimide J-Aggregate Donor-Acceptor Dyad. *Angew Chem Int Ed* 2019; 58: 12979–12983

## Biosketches



Nelson Ricardo Ávila Rovelo was born in Tegucigalpa, Honduras in 1992. He performed his bachelor degree in Chemical Engineering at the Universidad Nacional Autónoma de Honduras. He then pursued to obtain two master degrees, one in Polymer Science and the other in Sustainable Materials, from the consortium held between Université de Strasbourg and Albert-Ludwigs-Universität Freiburg. He is currently a first year PhD student at Institute Charles Sadron (CNRS) in Strasbourg (France), under the supervision of A. Ruiz-Carretero, where he performs his research on the in-situ control over morphology in organic electronic devices containing H-bonds.



Amparo Ruiz Carretero is a “Chargé de Recherche” at Institute Charles Sadron (CNRS) in Strasbourg (France). She studied Chemistry at the University of Castilla - La Mancha (Spain), where she obtained her PhD in 2009 under the supervision of Prof. A. de la Hoz and Dr. A. Sánchez. She spent a big part of her PhD in the group of Prof. E. W. Meijer and Prof. A. Schenning. After postdocs in the groups of Prof. S. Stupp (Northwestern University) and Prof. L. De Cola (University of Strasbourg), she obtained her current CNRS position in 2015. Her research interests include the study of hydrogen-bonded semiconductors, supramolecular chirality and the influence of magnetic fields in organic electronics