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Impact of molecular structure on intermolecular interactions and organic luminescence in supramolecular systems

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3 **Impact of molecular structure on intermolecular interactions and organic solid state**
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5 **luminescence in supramolecular systems**
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11
12 **Abstract:**

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14 Supramolecular chemistry provides a versatile approach to tune organic solid state
15 luminescence by controlling the molecular organization through weak interactions. In this
16 study, we have successfully tuned the solid state luminescence of 2-cyano-3(4-
17 (diphenylamino)phenyl)acrylic acid (CDPA) by co-crystallizing with substituted
18 pyridines. The position of methyl group on the pyridine (4-picoline, 3-picoline, 2-
19 picoline) has a dramatic effect on the supramolecular interactions formed, from usual
20 carboxylic acid-pyridine interactions to deprotonation of CDPA in the crystal lattice and
21 that allows to tune the CDPA solid state luminescence from 587 nm to 548 nm gradually.
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30 **Introduction**

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32 Solid state organic luminescent materials particularly with tunable luminescence are of
33 great interest in recent years, because of their applications in the field of optoelectronic
34 devices, including organic electroluminescence (EL), light-emitting diodes (LEDs), and
35 optical sensors.^[1] Organic molecules for example π -conjugated molecules show high
36 luminescence in dilute solution^[2] but become weakly luminescent in the solid state due to
37 the formation of less emissive species such as excimers and restrict the applications of
38 these molecules in high density optical systems.^[3] Strategies, such as the introduction of
39 bulky substituents or the synthesis of propeller-shaped luminescent molecules which
40 prevent close-packing in the solid state, have successfully lead to organic molecules that
41 luminesce in the solid state.^[4] The propeller-shaped triphenylamine and its derivatives
42 often show intense solid state luminescence and have been used in organic LEDs and
43 electroluminescent devices.^[5] The tuning of organic, solid state luminescence is mostly
44 achieved by the modification of substitutions on single molecules^[6] or the exploitation of
45 polymorphism.^[7] The latter approach is effective as the optical properties in the solid are
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controlled by molecular organization but it offers little predictability and the former requires interactive synthetic improvement.

The molecular arrangement of luminophores can be controlled through supramolecular interactions and this in turn can be used to tune or enhance the solid state luminescence.^[9] Although weak in organic compounds, supramolecular interactions such as H-bonding influence the energy levels of organic compounds and the stability of the excited state depending on the orientation of neighboring molecules.^[8] As an example, the supramolecular interactions of an organic luminescent acid has been effectively controlled by mixing it with amines and tuned the solid state luminescence.^[10] In general, deprotonation and protonation provides a simple strategy to switch or tune across a wide wavelength range, the emission of organic luminescent acids. We have recently reported the gradual shift of solid state luminescence from red to blue by utilizing unusual and subtle variations in the intermolecular interactions of 2-cyano-3(4-(diphenylamino)phenyl) acrylic acid (CDPA) with amines.^[11] The supramolecular luminescent host system of CDPA-piperidine exhibited CH₃CN selective luminescence switching. In this manuscript, we report the effect of molecular structure on the supramolecular interactions and optical properties of CDPA supramolecular luminescent systems with substituted pyridines. Supramolecular luminescence systems based on CDPA and 4-picoline (**1**), 3-picoline (**2**), and 2-picoline (**3**) are presented. The change of methyl position in the pyridine leads to different molecular arrangements of the CDPA in the solid state and a variety of supramolecular interactions. Most importantly, the change of CDPA molecular arrangement in the solid state is accompanied by changes in the solid state luminescence.

Results and Discussion

CDPA was synthesized by using the reported procedure¹² and crystallized from CH₃CN. The structural analysis of CDPA revealed a helical network structure formed through intermolecular interactions of the cyano nitrogen with carboxylic acid. Supramolecular luminescent systems were prepared by crystallizing CDPA with pyridines (1:1 mole ratio) in CH₃CN. It is worth noting that the crystalline products of CDPA supramolecular systems were mostly obtained from CH₃CN only. Ethyl acetate, methanol, ethanol, methylene chloride and toluene are the other solvents examined for

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3 preparation of CDPA based supramolecular systems. The supramolecular structure of
4 CDPA-pyridine (pKa = 5.14) forms with 1:0.5 molecule ratio of CDPA and pyridine. The
5 structural analysis reveals unusual supramolecular interactions in the crystal lattice.
6 Unexpectedly, the pyridine nitrogen was not seen to undergo intermolecular interactions
7 with CDPA carboxylic acid in the crystal lattice, instead all five carbon H-atoms of the
8 pyridine were involved in intermolecular H-bond interactions with different CDPA
9 molecules (Fig. 1). The disordered *para* carbon of pyridine is involved in C-H...O
10 interactions with the carbonyl oxygens of CDPA. The other four pyridine C-H form C-
11 H...NC H-bond interactions with the cyano nitrogen of different CDPA molecules. The
12 multiple pyridine interactions coupled with the carboxylic O-H...O-H intermolecular H-
13 bond interactions lead to the formation of CDPA dimers. Replacing the H atom of the
14 *para* carbon with a methyl group (4-picoline (pKa = 5.99), **1**) leads to the formation of
15 supramolecular structure with usual pyridine-carboxylic acid intermolecular interactions
16 (Fig. 2).^[13] **1** forms with 1:1 molecule ratio of CDPA and 4-picoline. The 4-picoline
17 nitrogen atoms and *ortho* carbon form N...H-O and O...H-C intermolecular interactions
18 with the carboxylic acid of CDPA in the crystal lattice of **1**. The same carbonyl oxygen
19 atom further interacts with the other *ortho* carbon of another 4-picoline molecule and
20 forms O...H-C interactions. The oxygen atom of the carboxylic hydroxyl group is
21 involved in the O...H-C interactions with the pyridine *meta* carbon along the z-axis. The
22 N...H-O and O...H-C intermolecular interactions, lead to the formation of a sheet-like
23 supramolecular structure in the *xz* plane.
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41 The single crystal X-ray analysis of **2** (3-picoline, pKa= 5.70) reveals another
42 interesting supramolecular structure. **2** forms with a 2:1 molecule ratio of CDPA and 3-
43 picoline molecule in the crystal lattice. The unit cell contains one molecule of 3-picoline
44 for every two molecules of CDPA. Of the two CDPA molecules only one is
45 deprotonated. In **2**, one of the deprotonated CDPA oxygen atoms forms O...H-N
46 intermolecular H-bond interactions with 3-picoline and the other oxygen rather than
47 forming any usual intermolecular H-bond interactions with the H atom of the *ortho*
48 carbons of pyridine, forms O...H-O interactions with a protonated CDPA carboxylic acid
49 (Fig. 3). The carbonyl oxygen of protonated CDPA forms O...H-C interactions with the
50 H atom of the *para* carbon of 3-picoline. The *ortho* carbon and the methyl carbon of 3-
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picoline is involved in the C-H...N interactions with a cyano group of a different deprotonated CDPA molecule. The cyano group of protonated CDPA did not form any supramolecular interactions. These multiple intermolecular H-bond interactions in **2** lead to the formation of a one-dimensional network structure along the y-axis. Despite repeated attempts, we could not obtain good quality single crystals of CDPA-2-picoline (Fig. 4, pKa = 6.00, **3**) from any solvent. It forms flake-like crystalline products from CH₃CN. The deprotonation of CDPA in **2** is rather surprising on consideration of the low basicity of 3-picoline, the weakest base among the picolines used. We have also observed similarly unexpected deprotonation of CDPA on using morpholine, the weakest base of the alicyclic amines used (piperidine, pyrrolidine and morpholine) in the preparation of supramolecular luminescent systems.^[11] As noted previously, there is a complex balance of forces at play in the solid state structures which go beyond or over-ride mere solution-based pKa considerations.

Powder X-ray diffraction (PXRD) patterns of **1-3** were measured and compared with the simulated powder pattern from single crystal data to confirm the purity of the sample (Fig. 5). The PXRD patterns of **1** and **2** are essentially the same as their respective simulated patterns (Fig. S1 and S2 in the supporting information) which indicates that the samples are not having polymorphism. A different PXRD pattern of **3** compared to CDPA, **1** and **2** suggests a different molecular arrangement in **3**.

The solid state luminescence spectra of supramolecular luminescent systems of **1-3** are shown in figure 6. CDPA exhibits strong luminescence in CH₂Cl₂ solutions with λ_{\max} at 603 nm and estimated quantum yield (Φ_f) 0.165 (on comparison with coumarin 6). Solid CDPA has similar luminescence intensity.^[11] Complexation with pyridine and picoline also show similar luminescence intensity compared to CDPA solid (Fig. S3 in the supporting information). However, the different supramolecular structures observed in the structural analysis were expected to lead to tuning of solid state luminescence. Powdered CDPA shows solid state luminescence at 587 nm. The subtle change of carboxylic acid H-bond interactions from O-H...NC in CDPA to O-H...O-H (Fig. 1) in pyridine blue shifts the luminescence from 587 nm to 565 nm. The usual pyridine-carboxylic acid H-bond formation in **1** (Fig. 2) further blue shifts the luminescence to 548 nm. **2** which has a deprotonated CDPA molecule in the crystal lattice should have further

blue shifted the solid state luminescence but the presence of a protonated CDPA molecule and the formation of O...H-O intermolecular interactions between protonated and deprotonated CDPA (Fig. 3) are more similar to the CDPA-pyridine supramolecular systems and led to solid state luminescence at 559 nm. **3** shows solid state luminescence at λ_{\max} 585 nm, a similar to that of CDPA powder, but the spectrum of **3** is sharper and narrower than that observed in the broad spectrum of CDPA.

Further information on the nature of the excited states was obtained by measuring the fluorescence lifetimes of CDPA in CH₃CN, CDPA and **1-3** powdered materials. Decays were monitored at the corresponding emission maxima. Structural information can also be obtained from the excited state lifetime since interactions with neighbouring molecules in the solid state can stabilize or destabilize the excited state. The luminescence profiles of CDPA in CH₃CN solution, powders of CDPA and CDPA-pyridine are shown in figure 7. Decays monitored in CH₃CN solution could be fitted monoexponentially, indicating a singlet excited state was exclusively formed. CDPA solids, CDPA-pyridine, and **1-3** showed biexponential decay, suggesting the involvement of multiple excited states and all had exhibited similar lifetimes (Table-1).

Table 1: Fluorescence lifetimes (τ_F) (Decay monitored at the corresponding λ_{\max} ; Excitation at 370 nm).

Compound	τ_1 (ns)	τ_2 (ns)	χ^2
CDPA-CH ₃ CN	1.733874		1.004136
CDPA-solid	9.56807	2.972946	1.038992
CDPA-pyridine	8.292209	1.887961	1.00473
1	10.58169	2.467983	1.040812
2	2.369388	10.02734	1.042162
3	2.621565	7.800654	1.050449

Conclusion

CDPA forms unusual intermolecular interactions with pyridines in the solid state. The position of methyl group on the pyridine (4-picoline, 2-picoline, 3-picoline) has a

dramatic effect on the supramolecular interactions formed, from usual carboxylic acid-pyridine interactions to deprotonation of CDPA. The usual pyridine-carboxylic acid intermolecular interactions in **1** blue shift the CDPA solid state luminescence from 587 nm to 548 nm. Unexpectedly 3-picoline, the weakest base of the picolines used, deprotonates the carboxylic acid of CDPA in the solid state. Thus, supramolecular interactions have successfully utilized to tune the CDPA solid state luminescence gradually from 587 nm to 548 nm.

Experimental Section

Synthesis and characterization:

Triphenylamine, cyanoacetic acid, POCl₃, anhydrous dimethyl formamide (99.8%), pyridine, 2-picoline, 3-picoline and 4-picoline were obtained from Aldrich and used as received. CDPA was prepared following the reported procedure.^[12] Elemental analyses were measured with a Perkin–Elmer 2400 II CHN analyzer.

General procedure for 1 – 3 preparation: A mixture of CDPA (100 mg, 0.29 mmol) and amine (0.3 mmol) was dissolved in acetonitrile (15 ml) and left to stand at room temperature. Crystals of **1-3** form after near complete evaporation of solvent. Above 90 % yield was obtained for **1– 3**.

Elemental analysis: (**1**) C₂₈H₂₃N₃O₂ (433.50): calculated. C 77.57, H 5.30, N 9.69; found. C 77.21, H 5.43, N 9.36.

(**2**) C₅₀H₃₈N₅O₄ (772.86): calculated. C 77.70, H 4.92, N 9.06; found. C 77.23, H 4.57, N 8.86.

(**3**) C₂₈H₂₃N₃O₂ (433.50): calculated. C 77.57, H 5.30, N 9.69; found. C 77.19, H 4.93, N 9.12.

X-ray Crystallography: PXRD measurements were recorded using Siemens diffraktometer-D500 at room temperature.

Single crystals were carefully chosen after they were viewed through a polarizing microscope. The crystals were glued to a thin glass fiber using an adhesive (cyano acrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The data collection was carried out at 150K and no extraordinary methods were employed, except that the crystals were smeared in NIH immersion oil to protect them

from ambient laboratory conditions. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS.^[14] The structure solution of all the complexes was carried out by direct methods, and refinements were performed by full-matrix least-squares on F^2 using the SHELXTL-PLUS^[15] suite of programs. All the structures converged to good R factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed on calculated position using appropriate HFIX options in Shelxtl and were refined isotropically.

Crystallographic data for 1: $C_{22}H_{16}N_2O_2$, C_6H_7N , $M = 433.49$, monoclinic, space group $P21/c$, $a = 7.301(3)$ Å, $b = 28.217(13)$ Å, $c = 13.270(5)$ Å, $\beta = 122.253(18)^\circ$, $V = 2312.0(17)$ Å³, $Z = 4$, $D_{\text{calcd.}} = 1.245$ g cm⁻³, $T = 150$ K, $\lambda_{(MoK\alpha)} = 0.71073$ Å, 23982 reflections measured, 4107 unique ($R_{\text{int}} = 0.0503$), Final R values: 0.0442, wR : 0.0981; *Crystallographic data for 2:* $4(C_{22}H_{16}N_2O_2)$, $4(C_{22}H_{15}N_2O_2)$, $4(C_6H_7N)$, $M = 3095.45$, monoclinic, space group $P21/c$, $a = 15.664(6)$ Å, $b = 9.406(4)$ Å, $c = 26.536(11)$ Å, $\beta = 94.340(8)^\circ$, $V = 3898(3)$ Å³, $Z = 1$, $D_{\text{calcd.}} = 1.318$ g cm⁻³, $T = 150$ K, $\lambda_{(MoK\alpha)} = 0.71073$ Å, 32991 reflections measured, 6801 unique ($R_{\text{int}} = 0.0823$), Final R values: 0.0684, wR : 0.1841. CCDC-755909 (for **1**) and CCDC-755908 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of Solid-State Luminescence and life-time Spectra: Luminescence spectra were recorded using Horiba Jobin Yvon Fluorolog instrument. Solid state luminescence was measured by spreading the powdered samples on a glass plate. The solids were excited at 370 nm. Fluorescence decay profiles of the samples were recorded using single photon counting spectrofluorimeter. The sample was excited by using nanodiodes (370 nm) and the decays were monitored at the corresponding emission maximum of the compounds. Data scan software was used for fitting the decay spectra ($\chi^2 = 1 - 1.3$) and yielded the fluorescence lifetimes.

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Figure Captions

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7 Figure 1: Crystal packing of CDPA-pyridine (a) and selected H-bond interactions in
8 the crystal lattice (b). Pyridine *para* carbon is disordered with nitrogen
9 atom. Only H atoms involved in H-bond interactions are shown; C (grey),
10 N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$ distances (Å)
11 are marked. Molecular structure of CDPA-pyridine with H-bond
12 interactions formed in the crystal lattice (c).
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19 Figure 2: Crystal packing of **1** (a) and selected H-bond interactions in the crystal
20 lattice (b). Only H atoms involved in H-bond interactions are shown; C
21 (grey), N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$
22 distances (Å) are marked. Molecular structure of **1** with H-bond
23 interactions formed in the crystal lattice (c).
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30 Figure 3: Crystal packing of **2** (a) and selected H-bond interactions in the crystal
31 lattice (b). Only H atoms involved in H-bond interactions are shown; C
32 (grey), N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$
33 distances (Å) are marked. Molecular structure of **2** with H-bond
34 interactions formed in the crystal lattice(c).
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41 Figure 4: Molecular structure of **3**.
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44 Figure 5: PXRD patterns of 1-3.
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47 Figure 6: Normalized solid state luminescence of (excitation $\lambda = 370$ nm).
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Impact of molecular structure on intermolecular interactions and organic solid state luminescence in supramolecular systems

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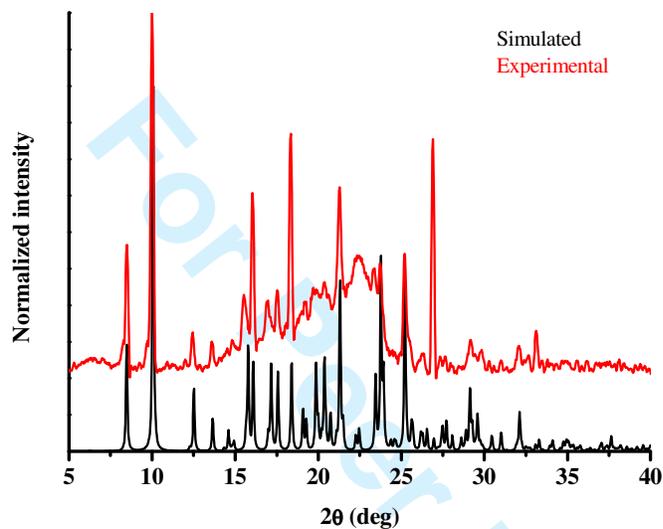


Figure S1. Simulated and experimental PXRD pattern of 1.

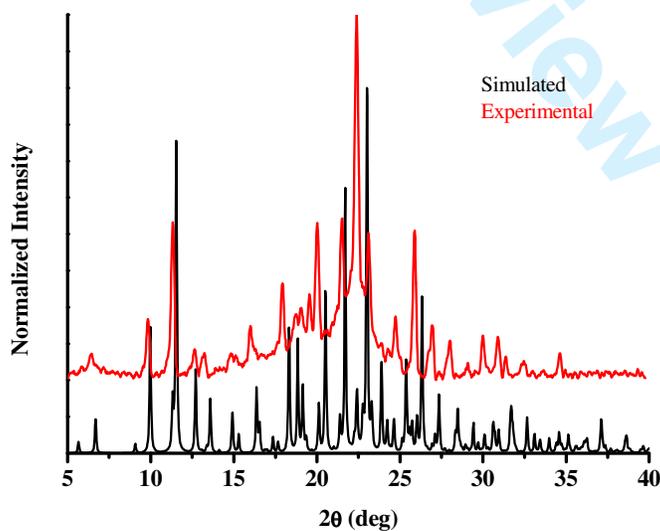


Figure S2. Simulated and experimental PXRD pattern of 2.

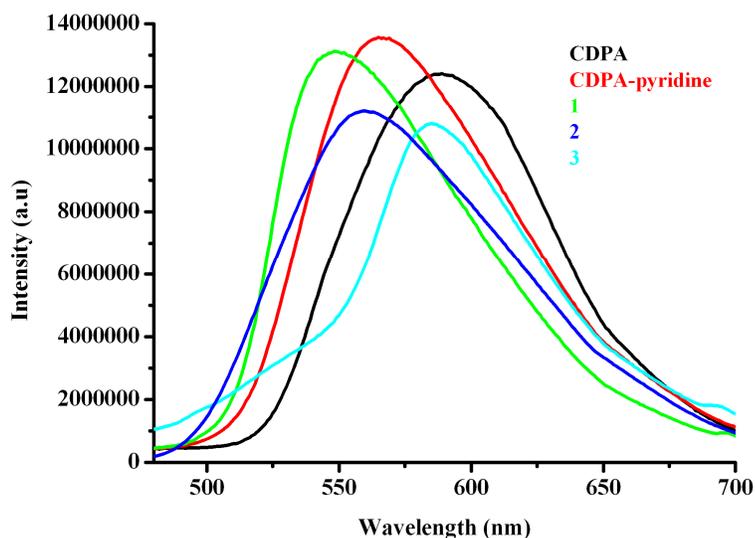
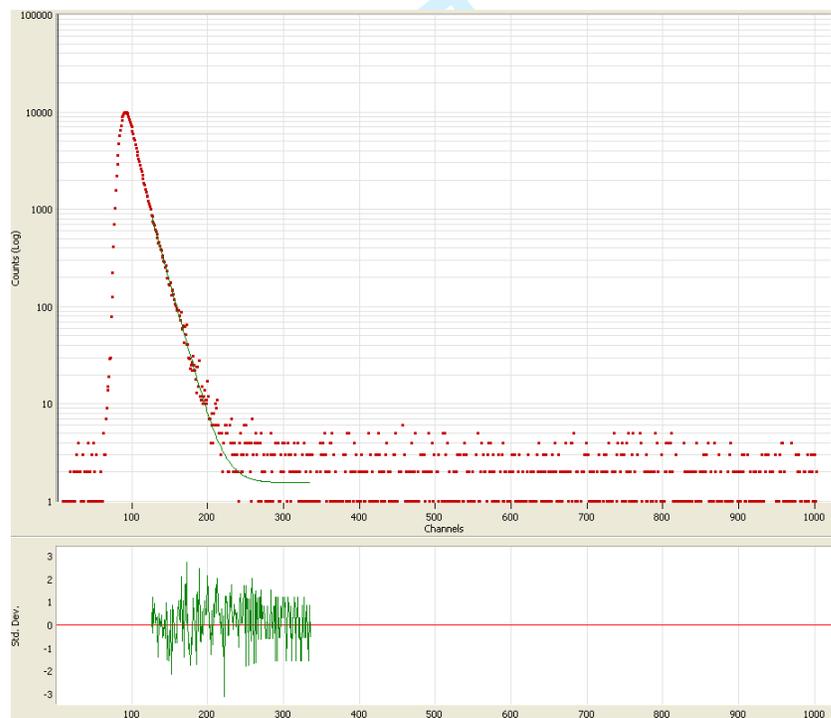


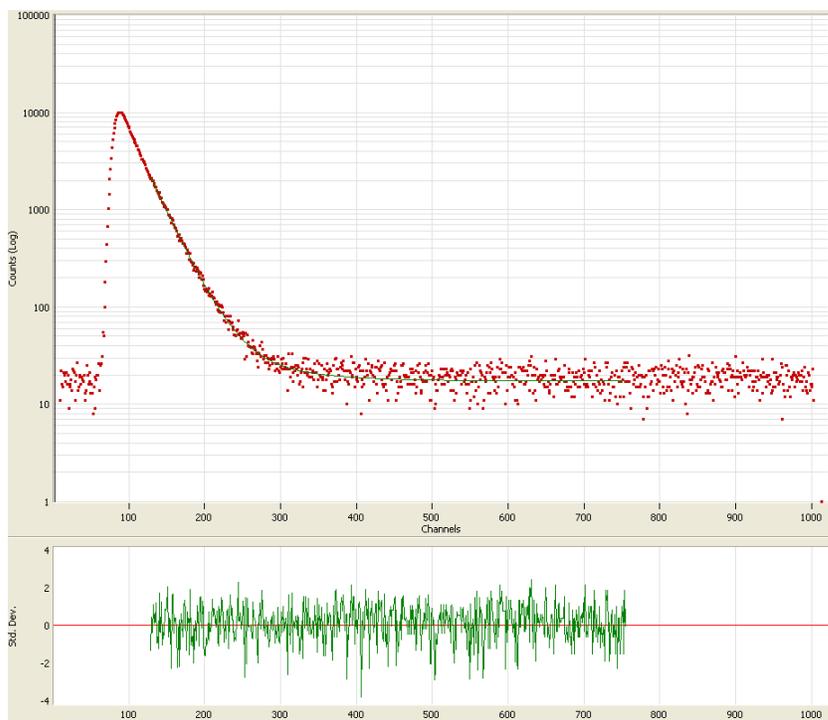
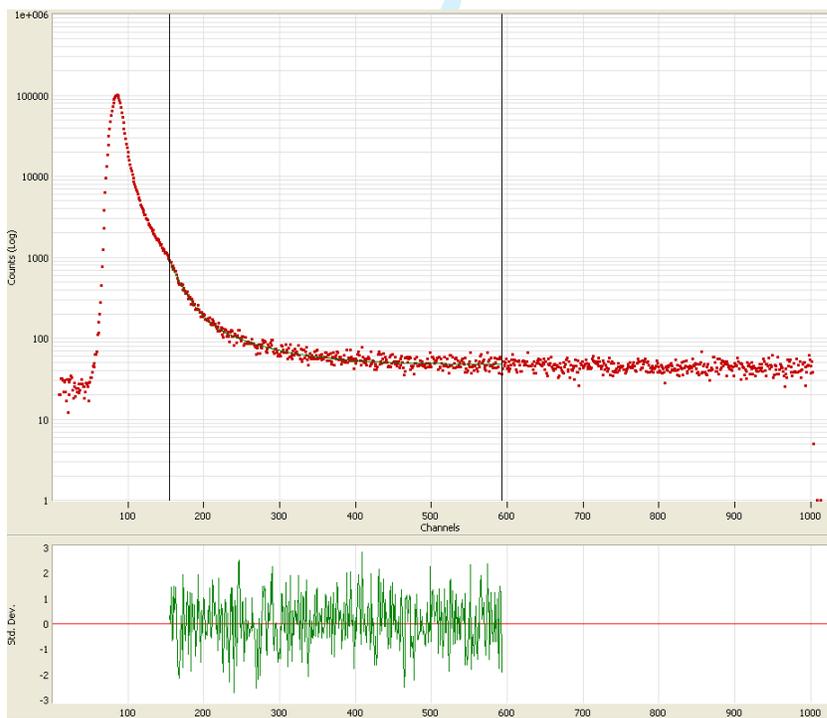
Figure S3. Comparison of luminescence intensity of CDPA, CDPA-pyridine, 1, 2 and 3.

Fluorescence decay profiles and fitting

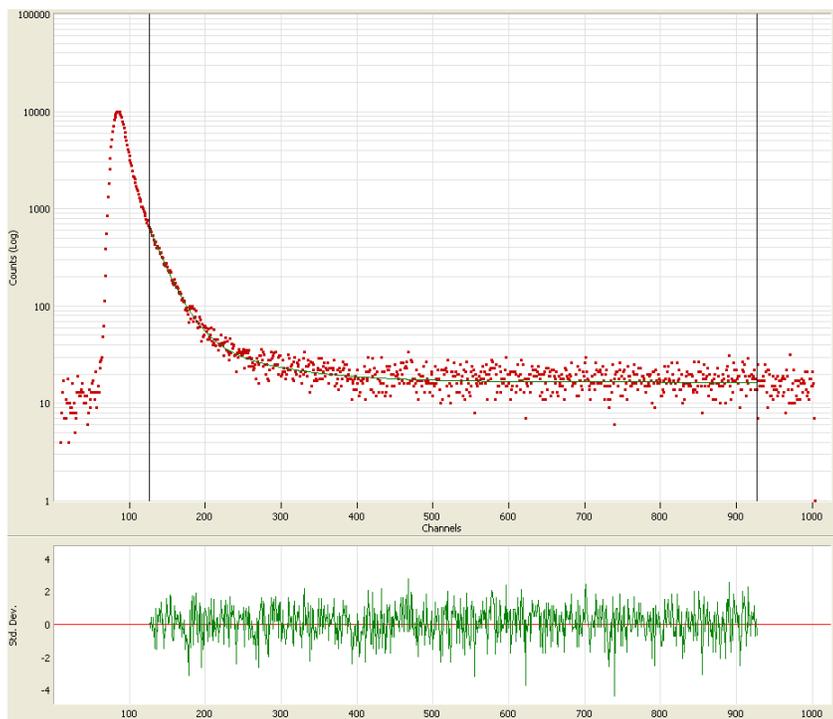
CDPA-CH₃CN



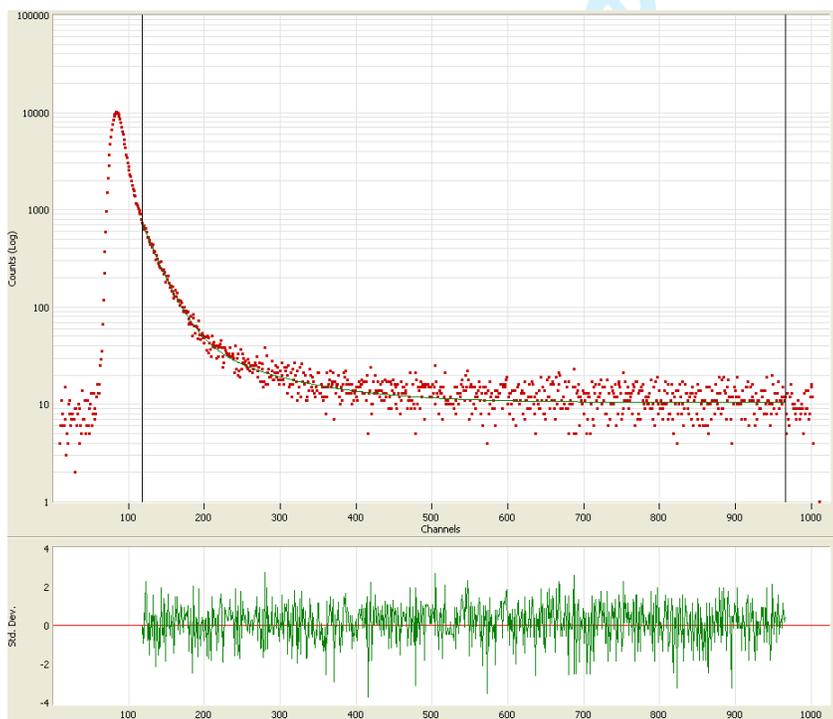
CDPA-solid

CDPA-
pyridine

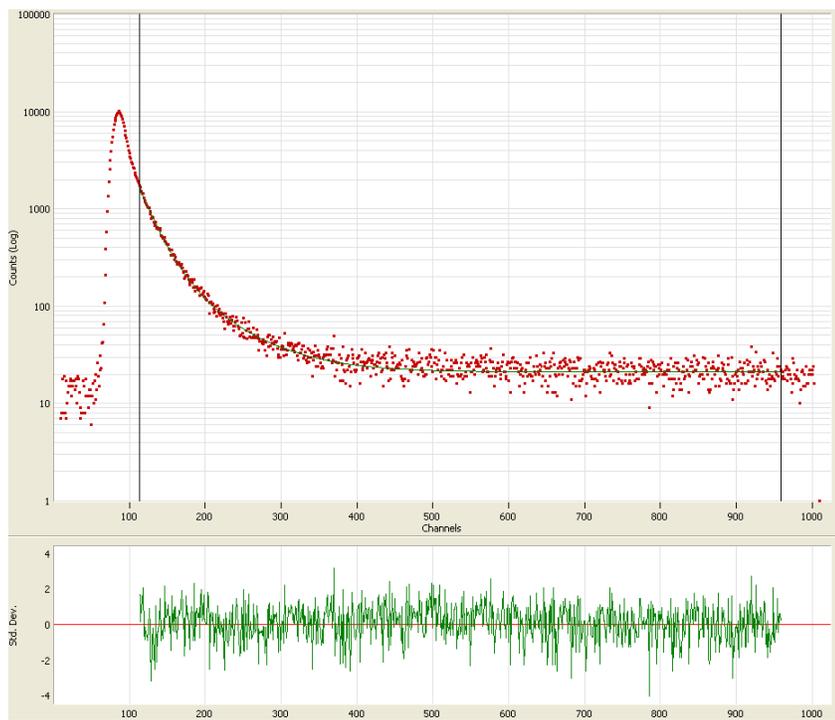
Compound-1

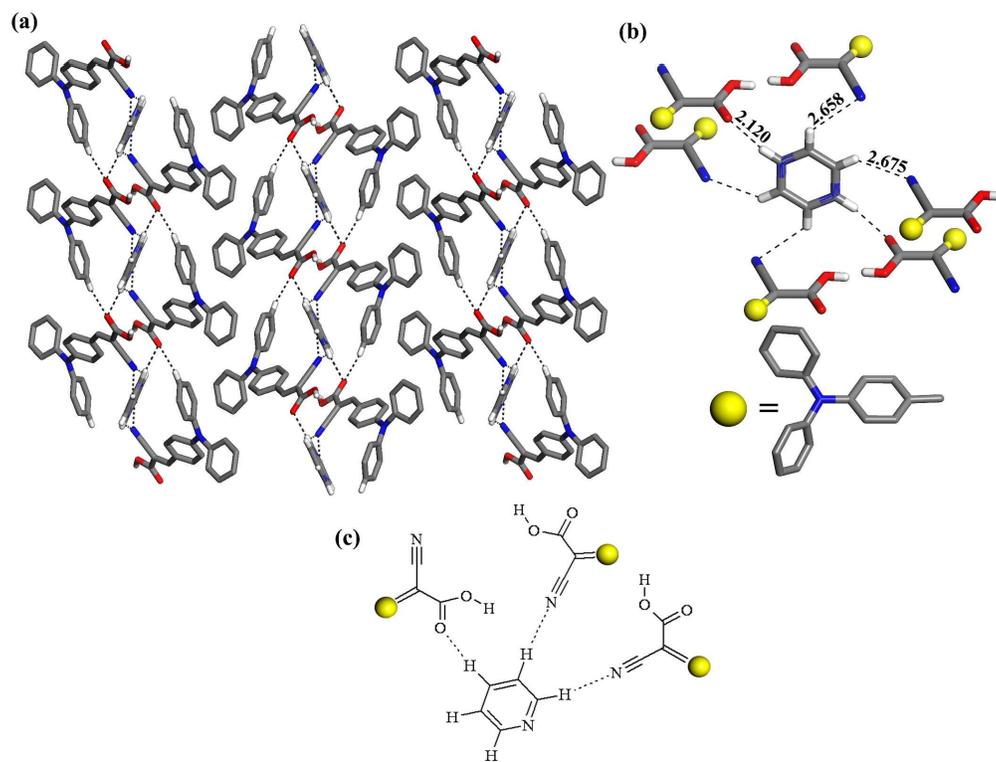


Compound-2

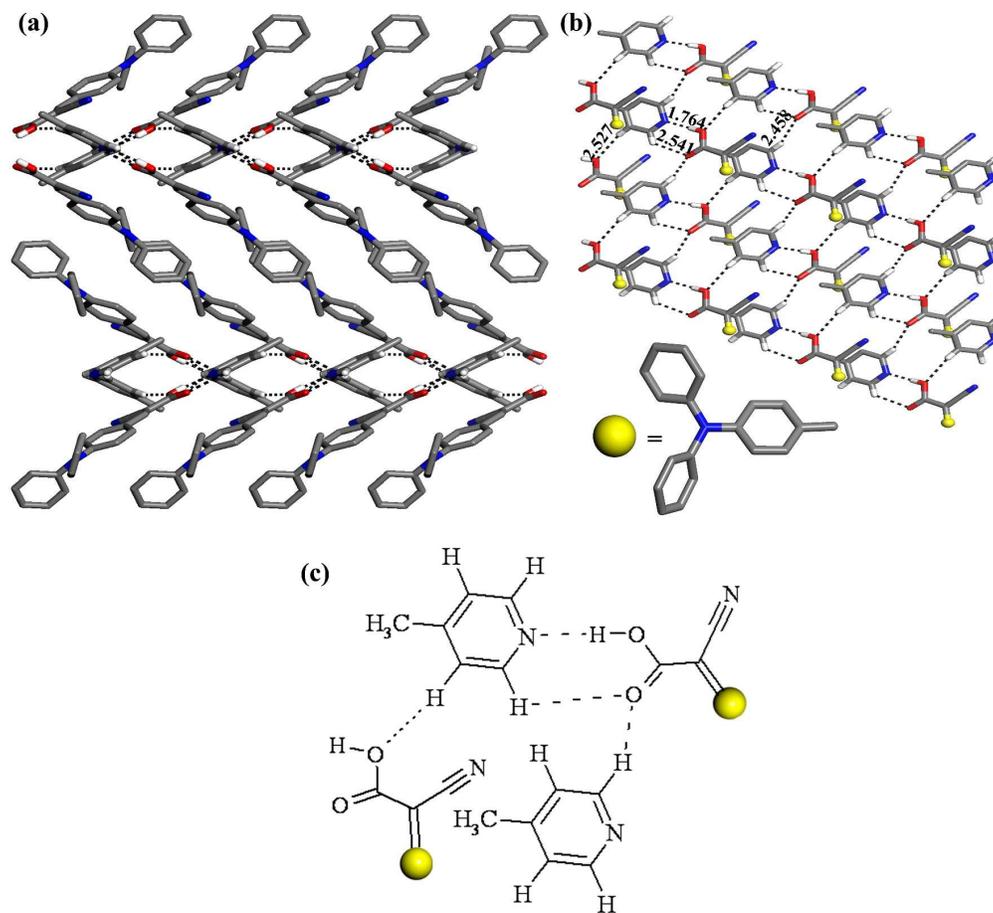


Compound-3

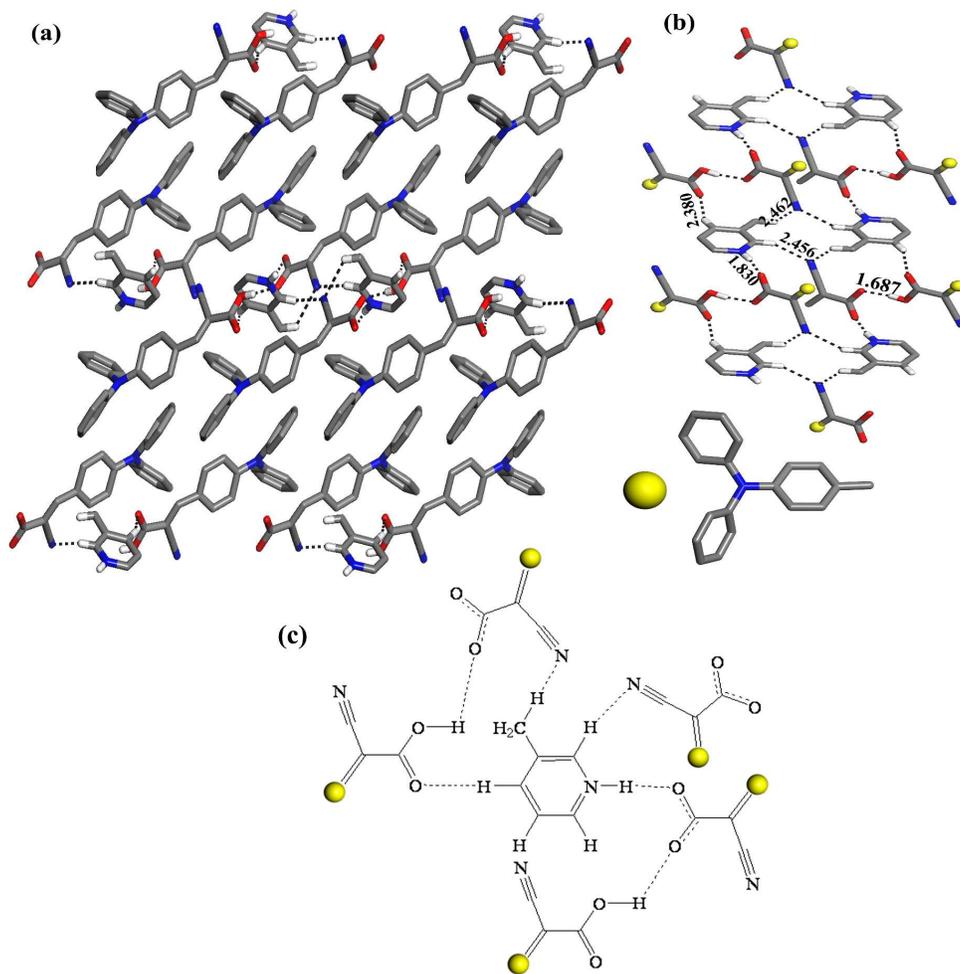




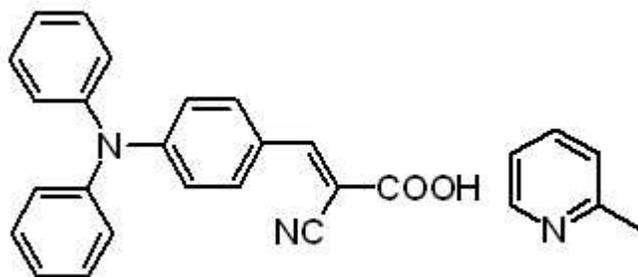
356x271mm (300 x 300 DPI)



223x208mm (400 x 400 DPI)

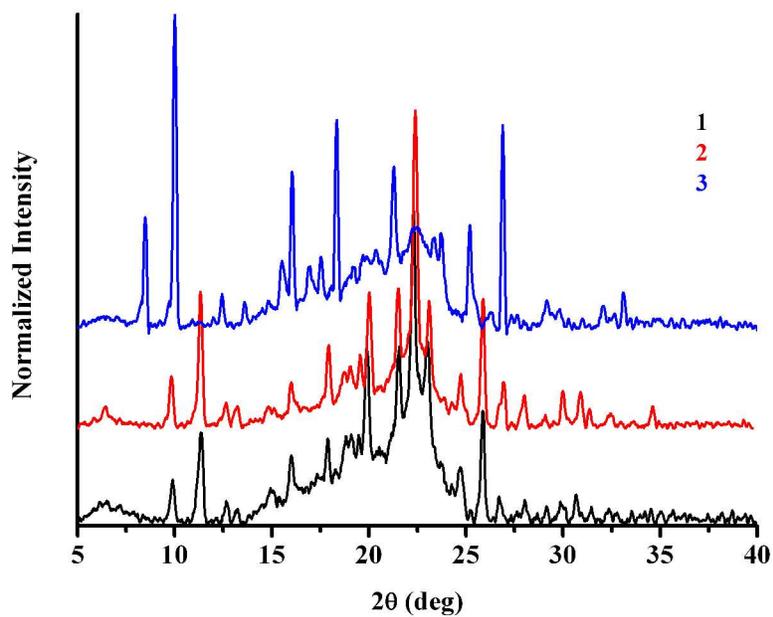


241x239mm (400 x 400 DPI)



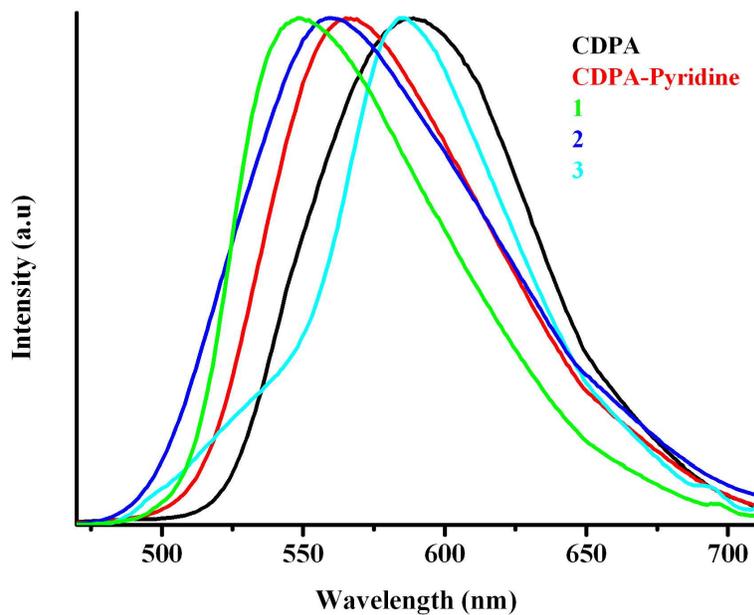
16x7mm (500 x 500 DPI)

or Peer Review

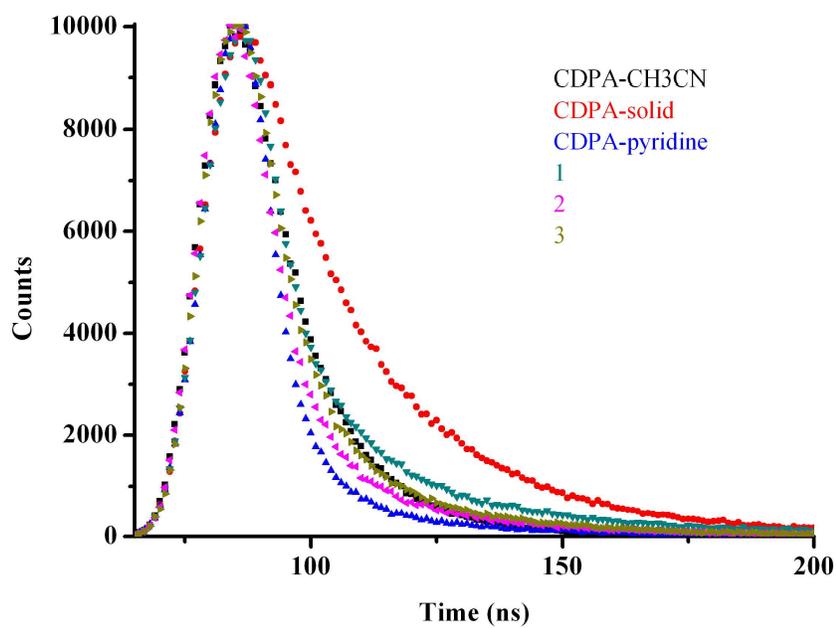


132x94mm (600 x 600 DPI)

review



113x81mm (500 x 500 DPI)



113x81mm (600 x 600 DPI)

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