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# 4,5,5-trimethyl-2,5-dihydrofuran based electron-withdrawing groups for NIR emitting push-pull dipolar fluorophores

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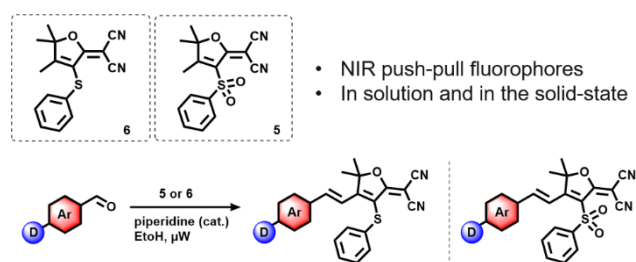
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## Abstract



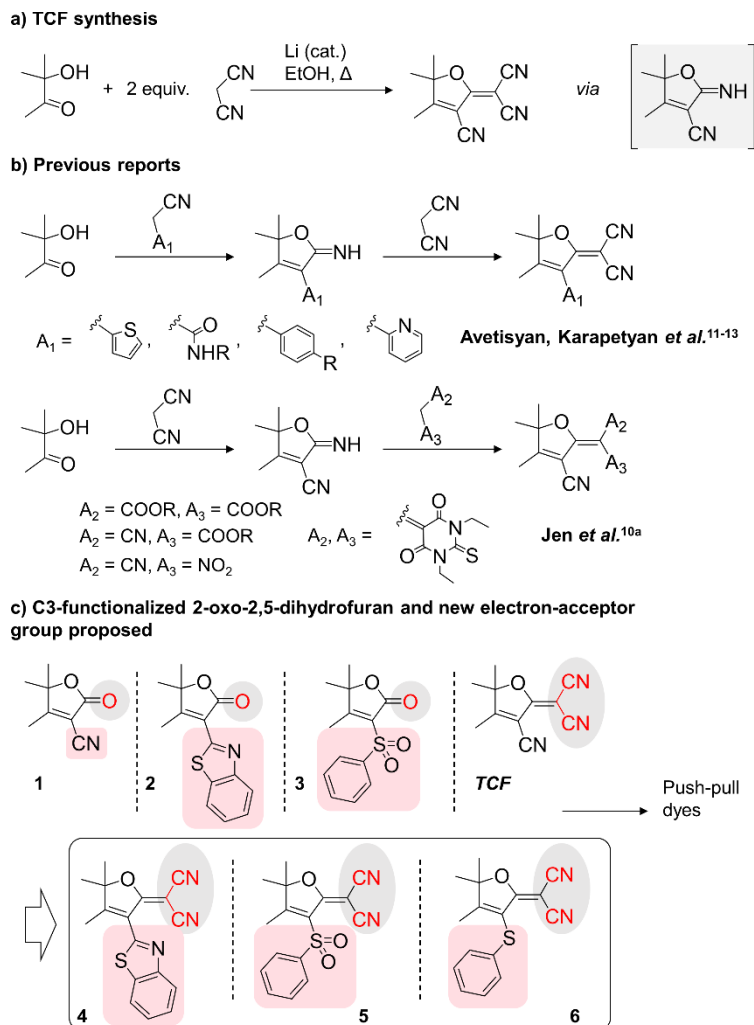
In the context of molecular engineering of push-pull dipolar dyes, we introduce a structural modification of the well-known electron-accepting group 2-dicyanomethylidene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF). Introduction of a (benzo[d]thiazol-2-yl) moiety failed and unexpected structures were obtained. On the other hand, phenylthio and phenylsulfonyl entities were successfully introduced at position 3 of the 2-(dicyanomethylene)-2,5-dihydro-furan ring giving access to new electron-acceptor groups and dipolar fluorophores displaying NIR emission in solution or solid state, brighter than their TCF analogues.

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## Introduction

*D*- $\pi$ -*A* push-pull chromophores, where *D* is an electron-donor group, *A* an electron-withdrawing group, covalently connected *via* a  $\pi$ -conjugated bridge, represent a fascinating class of dyes. They present unique spectroscopic properties ascribed to the intramolecular charge transfer following photon absorption, that can be easily tuned by the highly modular nature of the structure and rational adjustment of every single part.<sup>1</sup> Suitable combination of strong electron-donor and electron-acceptor groups allows shifting both absorption and emission properties to the near-infrared (NIR). This is a relevant key point for different applications including biological imaging, membrane polarity sensing, organic light-emitting diodes, organic photovoltaics, second-order nonlinear optical devices and, more recently, far-red solid state emitters,<sup>2</sup> in which push-pull dipolar dyes have been widely harnessed.

**TCF** (2-dicyanomethylidene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran) is one of the strongest electron-acceptor through the three nitrile groups, positioned in the same plane by the 2,5-dihydrofuran ring, and pulling electrons in approximately the same direction. First obtained in 1995 by Melikian and co-workers,<sup>3</sup> while exploring reactions aimed at the synthesis of new drug intermediates, **TCF** then emerged as acceptor group in push-pull dyes, revolutionizing the design of second-order nonlinear optical dyes.<sup>4,5</sup> It was later used for designing small red-emitting fluorescent push-pull dyes,<sup>2a, 2b, 6</sup> for efficient far-red solid state emitters,<sup>2i, 7</sup> or as acceptor dyes in thermally activated delayed fluorescent solution-processed NIR OLEDs.<sup>8</sup> **TCF** is easily obtained from 3-hydroxy-3-methylbutan-2-one and two equivalents of malononitrile by a two-steps sequence involving the formation of a cyclized imino-lactone intermediate, 2-imino-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (Figure 1a). By changing the  $\alpha$ -hydroxyketone precursor, the two methyl groups at position 4 can be independently replaced by other alkyl group, phenyl or perfluoroalkyl groups,<sup>9</sup> allowing size, shape and electronic character variation, thereby enhancing the electron-withdrawing character.<sup>5</sup> However, very few examples of dipolar chromophores based on these original and powerful electron-withdrawing groups are described, and exclusively chromophores exploited for their 2<sup>nd</sup> order non-linear optical properties.<sup>10</sup> Some **TCF** analogues in which one (or more) nitrile group is replaced by other electron-withdrawing entities were described. Avetisyan and co-workers prepared various 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethyl-3-furancarboxamide rings,<sup>11</sup> 2-dicyanomethylene-4,5,5-trimethyl-3-phenyl-2,5-dihydrofuran<sup>12</sup> and 2-dicyanomethylene-4,5,5-trimethyl-3-thienyl-2,5-dihydrofuran,<sup>13</sup> in which the nitrile in position 3 is replaced by amide groups or a thienyl ring respectively (Figure 1b). Villemin and Liao reported the use of focused microwave heating, rather than conventional heating, to synthesize the 2-imino-3-cyano-4,5,5,5-trimethyl-2,5-dihydrofuran intermediate, before reaction with a second malononitrile molecule.<sup>14</sup> Jen and Dalton then applied the same concept to isolate the reactive intermediate. They described the step-wise synthesis of various 2,5-dihydrofuran derivatives (2-(1-ethoxycarbonyl-1-cyano)methylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, 2-(1-cyano-1-nitro)methylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran or 5-(3-cyano-4,5,5-trimethyl-2,5-dihydro-2-furanyl)-1,3,-diethyl-2-thiobarbituric acid), by condensation reaction with activated methylene compounds (Figure 1b),<sup>10a</sup> but did not go any further. To the best of our knowledge, no chromophore incorporating these new electron-acceptor patterns was ever reported. Only dyes with one carboxylic (or carboxamide) groups in place of one nitrile in position 2 are known.<sup>15</sup>

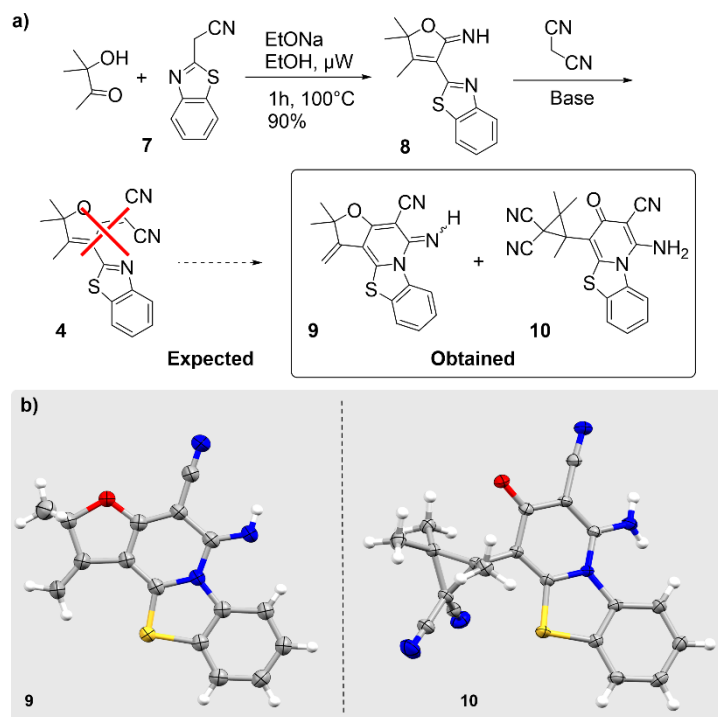


**Figure 1.** a) *TCF* synthesis, b) structure modifications described in literature, c) structures of C3-functionalized 2-oxo-2,5-dihydrofuran ring and of the new electron-acceptor groups proposed.

## Results and Discussion

We recently described 2-oxo-2,5-dihydrofuran derivatives bearing electron-withdrawing group at the C3 position, namely 3-(cyano)-4,5,5-trimethylfuran-2(5*H*)-one **1**, 3-(benzo[*d*]thiazol-2-yl)-4,5,5-trimethylfuran-2(5*H*)-one **2** and 4,5,5'-trimethyl-3-(phenylsulfonyl)furan-2(5*H*)-one **3** (Figure 1c), and their incorporation as electron acceptors in various push-pull dipolar structures giving interesting far-red fluorophores emitting in solution and especially in the solid state.<sup>7b, 16</sup> In light of this development, we now wish to extend this engineering to the preparation of 2-(dicyanomethylene)-2,5-dihydro-furan ring with either benzo[*d*]thiazol-2-yl, phenylsulfonyl installed at position C3 to enrich the collection of strong electron-acceptor groups (**4** and **5** respectively, Figure 1c). 2-(dicyanomethylene)-2,5-dihydro-furan ring bearing a phenylthio group (compound **6**, Figure 1c), obtained during the synthesis of **5** was

also used as electron-accepting group that can be incorporated in original push-pull dipolar structure able to emit in the far-red/NIR in the solid state or in solution.



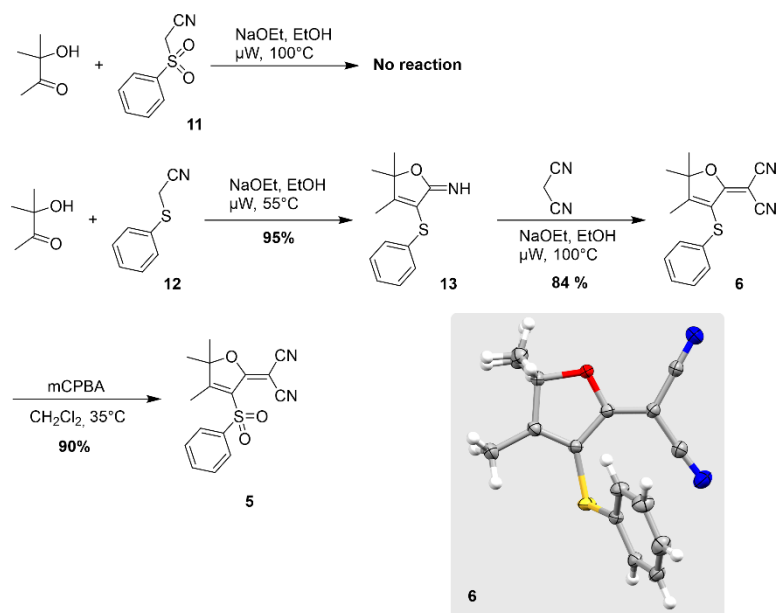
**Figure 2.** a) Reaction conditions for the incorporation of a benzo[d]thiazol-2-yl moiety and b) X-ray crystal structures of the unexpected condensation products **9** and **10** obtained from 4,5,5-trimethyl-3-(benzo[d]thiazol-2-yl)-2(5H)-furanimine (ORTEP view with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radius).

We first attempted to obtain compound **4** from 3-hydroxy-3-methyl-2-butanone, 2-benzothiazoleacetonitrile and malononitrile by the two-steps reaction sequence isolating the imino-lactone intermediate (Figure 2a). So, reaction of one equivalent of 2-benzothiazoleacetonitrile **7** with 3-hydroxy-3-methyl-2-butanone in presence of sodium ethanolate in acetonitrile and using focused microwave heating gave the corresponding 4,5,5-trimethyl-3-(benzo[d]thiazol-2-yl)-2(5H)-furanimine **8** in very good isolated yield (90 %, Figure 2a). Subsequent reaction with malononitrile, on the other hand, was rather sluggish, complete conversion of the starting imino-lactone requiring long reaction time, and systematically failed to produce the desired 2-(dicyanomethylene) compound **4**. Instead, two unknown products **9** and **10** were obtained in various proportions depending on the reaction condition (see SI). Compound **9** is a yellow fluorescent solid. An ion  $[M+H]^+$  of mass 308 on mass spectrometry and <sup>13</sup>C NMR indicated the addition of one malononitrile, but <sup>1</sup>H NMR pointed to the persistence of an imine function (signals at 9.67 and 9.69 ppm, Figure SI-1) and of two vinylic protons resonating at 4.92 and 5.25 ppm, respectively. **10** is white solid. <sup>1</sup>H/<sup>13</sup>C NMR spectra showed the existence of three different -CH<sub>3</sub> groups (at 1.29/21.2 ppm, 1.42/14.7 ppm and 1.49/17.8 ppm, Figure SI-2), whereas mass spectrometry gave 373 for  $[M+H]^+$ , which corresponds to the addition

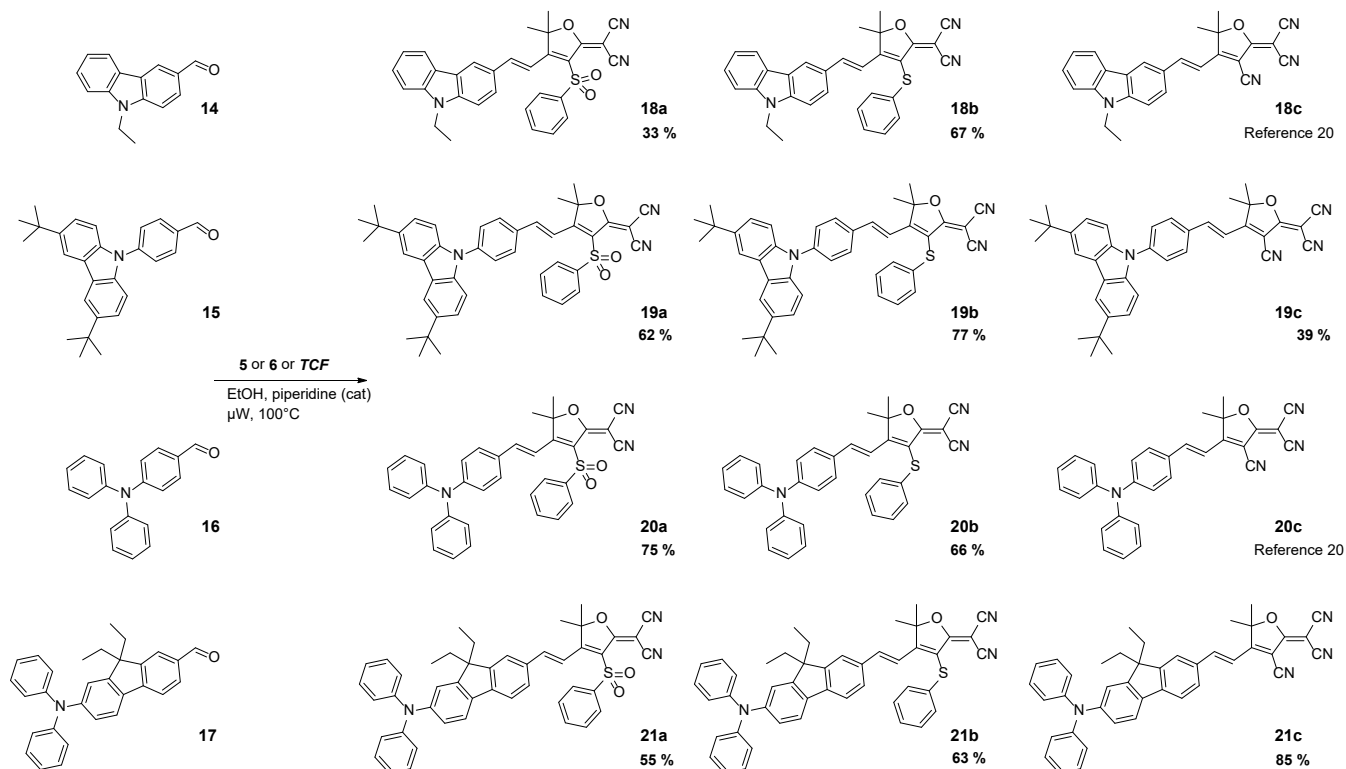
of two malononitrile entities. More surprisingly the infrared spectrum displayed a typical C=O vibration at 1592 cm<sup>-1</sup>, along with the C≡N absorption at 2212 cm<sup>-1</sup>. Compounds **9** and **10** were crystallized from ethanol and the structure was revealed by X-ray diffraction analysis (Figure 2b, Table SI-2 and SI-3). **9** is characterized by a fully planar four-fused-rings structure incorporating a bridgehead nitrogen atom, and an exocyclic C=C double bond, resulting from the addition of one molecule of malononitrile on the imino-lactone as expected, followed by ring-closure reaction of the benzo[d]thiazol-2-yl nitrogen on one of the two C≡N group and hydrogen transfer. Likewise, a three-fused-rings structure and a bridgehead nitrogen atom is also to be found in the structure of **10**. However, 1,4-addition of a second molecule of malononitrile induced a structural rearrangement with formation a cyclopropyl ring and opening of the furan ring explaining the NMR and IR data (see partial NMR attribution of **10** in SI). Those compounds exhibit absorption maxima at 407 nm for **9** and 428 nm and 397 nm for **10** (Figure SI-4). Both are also emitting with maxima at 478 nm (in CHCl<sub>3</sub>) and 469 nm (in DMSO) respectively (Stokes' shifts Δ<sub>v</sub> ~ 2440 cm<sup>-1</sup> and 3865 cm<sup>-1</sup>) and interesting quantum yield (Φ<sub>f</sub> = 82 % in CHCl<sub>3</sub> and 28 % in DMSO, resp. Table SI-1) Unfortunately, rapid degradation under irradiation was observed in the case of **9** preventing further use.

Following this dissatisfaction, we preferred focusing on the other electron-acceptor group **5**. However, in this case, reaction of 2-(phenylsulfonyl)-acetonitrile **11** and 3-hydroxy-3-methylbutan-2-one in basic conditions using microwave or conventional heating systematically failed to give the imino-lactone intermediate. By lowering the temperature, no reaction takes place and the starting materials were systematically recovered. The lower reactivity of 2-(phenylsulfonyl)-acetonitrile compared with malononitrile may be explained by the higher stability of the anion due to the stronger inductive effect of the sulfonyl group in opposition to the nitrile group, as already observed on bis(perfluoroalkylsulfonyl)methanes and on perfluoroalkylsulfonyl-acetonitrile derivatives.<sup>17</sup> While Ferraris and Torres forced the Knoevenagel condensation between perfluoroalkylsulfonyl-acetonitrile and strained ketone by using combination of a Grignard reagent of the methylene compound and TiCl<sub>4</sub>-activation of the ketone,<sup>18</sup> we preferred to use a step-wise approach from 2-(phenylthio)-acetonitrile **12** with a last step of oxidation from thioether to sulfone (Scheme 1). So reaction of 2-(phenylthio)-acetonitrile **12** with 3-hydroxy-3-methylbutan-2-one in ethanol in presence of sodium ethoxide using microwave heating proceeded smoothly and gave access to the corresponding imino-lactone **13**. Excess malononitrile added stepwise was nevertheless necessary to obtain 2-(dicyanomethylene)-3-phenylthio-4,5,5-trimethyl-2,5-dihydro-furan **6**, whose structure was confirmed by X-ray diffraction on single crystal. The 2-(dicyanomethylene)-2,5-dihydro-furan motive is fully planar with the phenyl ring forming a 70° angle to it (Scheme 1) Finally, oxidation with two equivalents of *m*-CPBA afforded the desired compound **5** in overall 72% yield for the three steps.

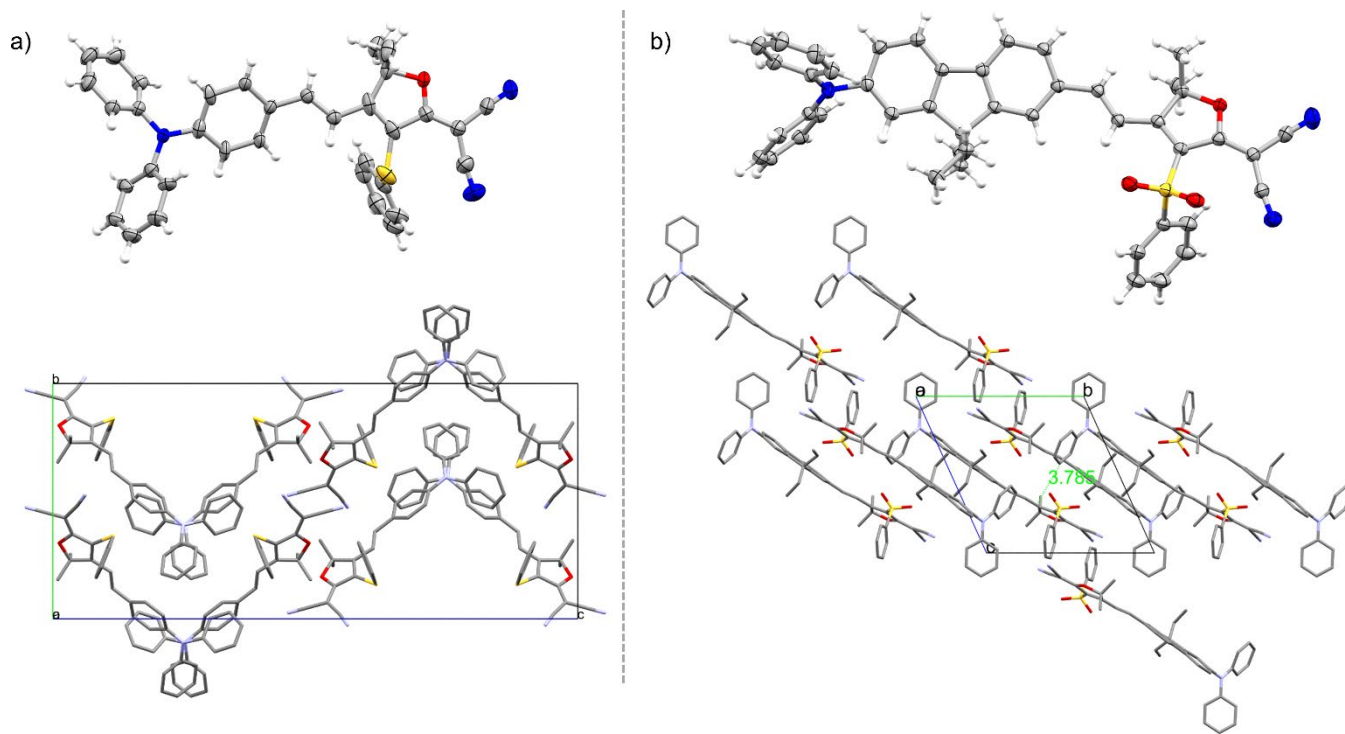
Having **5** in hand we turned our attention to incorporation into push-pull dipolar structures **18a-21a** by simple Knoevenagel reaction with various electron-donor counter-part and as so many aromatic aldehydes **14-17** chosen as classical representative examples and for their ease of access. For comparison, analogue dyes build on 2-(dicyanomethylene)-3-phenylthio-4,5,5-trimethyl-2,5-dihydro-furan **6** (**18b-21b**) and on *TCF* (**18c-21c**) were also synthesized. Dyes **18a/c-21a/c** (Scheme 2) were therefore obtained in 33 to 85 % yield. All compounds were fully characterized. It has to be noted that all *phenylsulfonyl* and *phenylthio* compounds are perfectly stable on standing. In particular, no oxidation to sulfoxide was observed for the *phenylthio* derivatives during synthesis or purification.<sup>19</sup>



**Scheme 1.** Synthesis of electron-accepting building blocks **5** and **6**, and crystal structure of **6** (ORTEP view with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radius).



**Scheme 2.** Synthesis of push-pull dipolar fluorophores **18a/b-21a/b** based on the new electron-accepting building blocks and of the TCF analogues **18c-21c**. Conditions: **14-17** (1.1 equiv.), **5** or **6** or **TCF** (1equiv.), piperidine (cat.), abs. EtOH,  $\mu$ W, 100°C, 30 min. to 1 h. Yields refer to the isolated products.



**Figure 3.** a) Crystal structure of **20b**: ORTEP view with 50% probability displacement ellipsoids (H atoms are shown as spheres of arbitrary radius) and crystal packing viewed down crystallographic *a* axis showing the herringbone pattern; b) Crystal structure

of **21a**: ORTEP view with 50% probability displacement ellipsoids (H atoms are shown as spheres of arbitrary radius) and crystal packing viewed down crystallographic *a* axis showing the brickwork-like pattern.

Sub-millimeter size crystal suitable for X-ray diffraction were obtained for compounds **20a**, **20b**, **21a** and **21b** bearing the two new electron-acceptor groups, and the structures were resolved. Crystallographic data are given in Table 1, whereas refinement parameters basic structural parameters, selected distances and dihedral angles are compiled in SI (Tables SI-4 and SI-5, Figure SI-8). Compounds **20a** and **21b** crystallized in the monoclinic  $P2_1/c$  space group (with  $Z = 4$ ), compound **21a** in the triclinic  $P\bar{1}$  space group ( $Z = 2$ ) and compound **21b** in the orthorhombic  $Pbca$  space group ( $Z = 8$ ). The conjugated systems of the four molecules are almost planar with twenty atoms (for compounds **20a** and **20b**) or twenty-seven atoms (for compounds **21a** and **21b**), including the *N*-donor, the sulfur atom and all the nitrile  $-C\equiv N$  functions, forming the main molecular plane. The average puckering amplitude to the mean plane  $\Delta$  ranged from 0.172 Å (**20b**) to 0.217 Å (**21b**) with a maximum amplitude for the most distorted structure of 0.791 Å (one of the nitrile group of compound **21b**). The dihedral angles  $\theta$  measured between the phenyl (**20a**, **20b**) or the fluorenyl (**21a**, **21b**) ring and the five-membered dihydrofuran ring ranged from 11.8° (**20a**) to 24.5° (**20b**), indicative of a strong conjugation between the donor and the acceptor end. The two phenyl rings on the *N*-donor atom adopt a classical propeller type conformation, whereas the two diethyl groups of the fluorenyl compounds arrange on both side of the molecular plane. Finally, the phenyl ring of the *phenylthio*- and *phenylsulfonyl*- function is placed practically perpendicular to the average plane (angle ranging from 63.5° for **21b** to 89.8° for **20a**).

**Table 1.** Crystal data for **20a**, **20b**, **21a** and **21b**

	<b>20a</b>	<b>20b</b>	<b>21a</b>	<b>21b</b>
CCDC	1894855	1894857	1894856	1894858
Formula	C <sub>35</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> S	C <sub>35</sub> H <sub>27</sub> N <sub>3</sub> OS	C <sub>46</sub> H <sub>39</sub> N <sub>3</sub> O <sub>3</sub> S	C <sub>46</sub> H <sub>39</sub> N <sub>3</sub> OS
Mr (g.mol <sup>-1</sup> )	569.68	537.68	713.90	681.90
Cryst. Syst.	Monoclinic,	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	22.307 (3)	11.1584 (17)	11.8120 (13)	22.113 (3)
b (Å)	9.2796 (9)	15.1108 (17)	12.9977 (16)	9.141 (8)
c (Å)	14.2356 (17)	33.728 (4)	13.5311 (15)	19.164 (2)
$\alpha$ (°)			65.759 (11)	

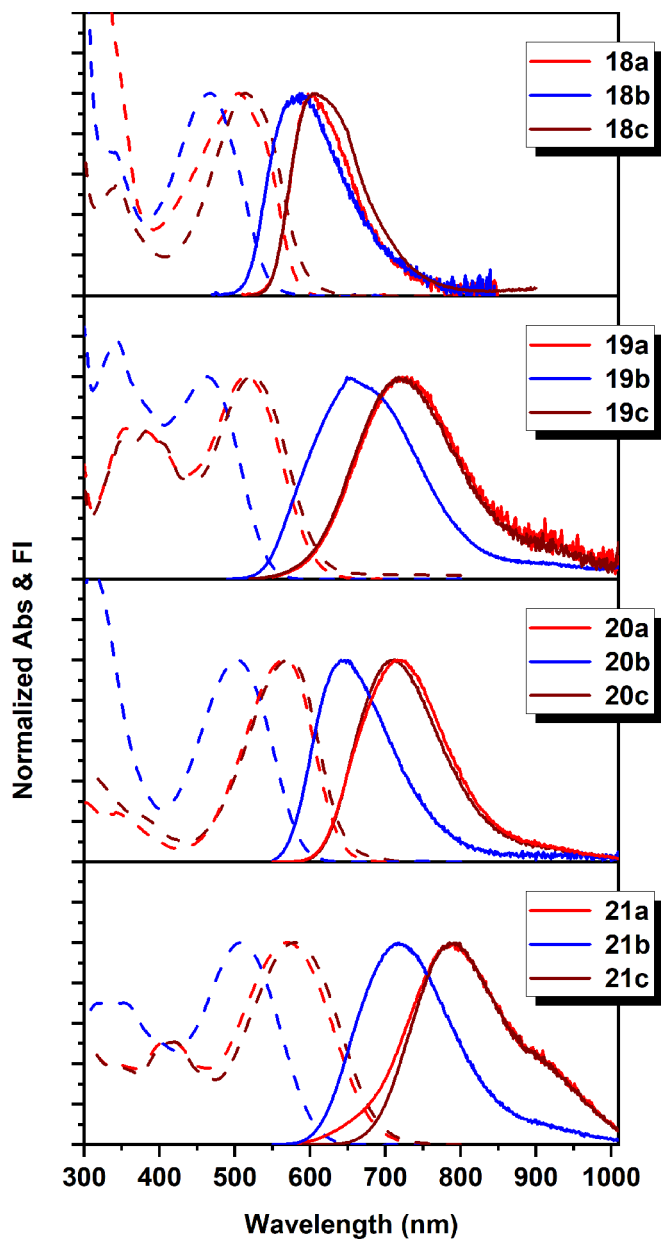
$\beta$ (°)	104.766 (14) <sup>o</sup>		79.321 (10)	105.731 (11)
$\gamma$ (°)			87.886 (10)	
V (Å <sup>3</sup> )	2849.5 (6)	5687.0 (13)	1859.7 (4)	3729 (3)
Z	4	8	2	4
T (K)	150	260	150	150
F(000)	1192	2256	752	1440
D (g.cm <sup>-3</sup> )	1.328	1.256	1.275	1.215
$\mu$ (mm <sup>-1</sup> )	1.34	0.15	0.13	0.13
Crystal size (mm)	0.31 × 0.06 × 0.02	0.41 × 0.34 × 0.13	0.42 × 0.23 × 0.17	0.29 × 0.16 × 0.09

Crystal packing revealed herringbone (**20b**, Figure 3a) or double herringbone patterns (**20a**, **21b**, Figures SI-9 and SI-10) created by two or four molecules arranged in “V” or by broken lines of molecules. For compound **21a**, the two molecules in the cell are stacked (distance between the two molecular mean plane 3.785 Å), but slipped away from ca 3.11 Å along the main molecular axis creating a brickwork-like patterns (Figure 3b). Such packing closely resemble what was observed for similar structural solid state emitter<sup>2i, 7b, 16, 20</sup> and may be related to the good emission properties observed in the solid state for these two compounds (*vide infra*).

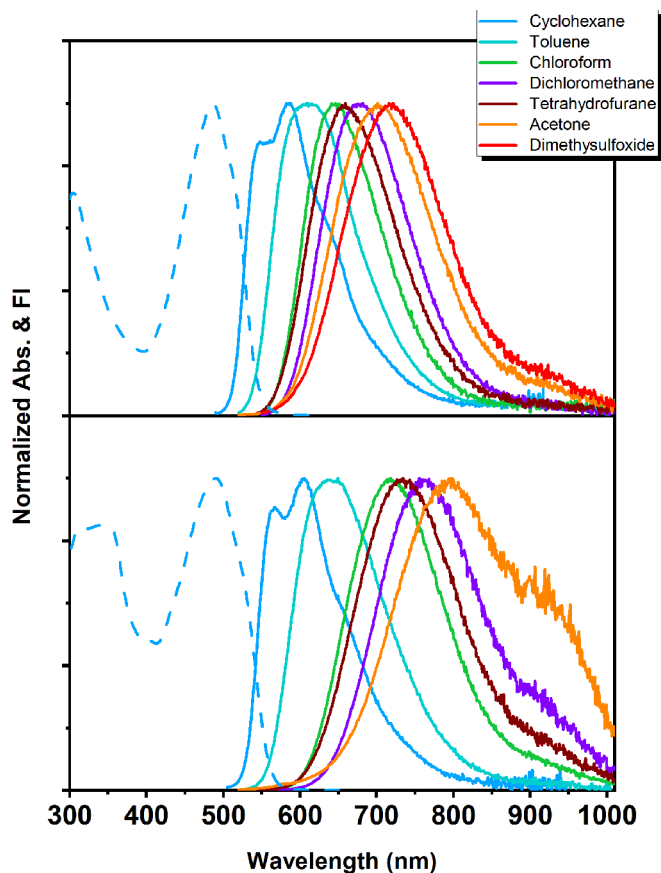
The spectroscopic properties (absorption and emission) of all compounds were studied in diluted chloroform solution first, a solvent of moderate polarity (Figure 4), then in solvents of various polarity (Figure 5 and Figures SI-11 to 46). Data are presented in Table 2 and in SI. Logically, all compounds present a broad absorption in the visible characteristic of induced charge transfer (ICT). This includes **19a-c** based on 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)- donor moieties, which is in contradiction with a recent report stating that “the CT absorption band was almost negligible” for compound **19c**.<sup>8</sup> *Phenylsulfonyl*- ( $\sigma_p = 0.68$ ) and *cyano*- ( $\sigma_p = 0.66$ ) have similar Hammett substituent constants  $\sigma_p$ ,<sup>21</sup> indicating similar electron-withdrawing capacity while thiophenyl- ( $\sigma_p = 0.07$ ) is a much weaker electron-accepting group. This is reflected in the UV/vis absorption spectra of dyes **18a/c-21a/c** (Figure 4), with a pronounced bathochromic shift in absorption when replacing  $-\text{SC}_6\text{H}_5$  by  $-\text{SO}_2\text{C}_6\text{H}_5$  or  $-\text{CN}$  for the same  $\pi$ -bridge and electron-donor group. On the other hand, *phenylsulfonyl*-compounds display absorption maxima that compared directly with the **TCF** analogues. These observations can be made regardless of the solvent as presented in figures SI-11 to SI-46 showing the weak variation of the absorption as a function of solvent polarity. So, the absorption maxima in chloroform ranged from 463 nm (**19b**) to 509 nm (**21b**) for the *thiophenyl*- derivatives and from 506 nm (**18a**) to 580 nm (**21c**) for the *phenylsulfonyl*- and *cyano*-ones (Table 2).

The photoluminescence of **18a/c-21a/c** in chloroform (Figures 4 and SI-11 to 46) observed following excitation in the main CT band varies considerably from one series of compounds to another. Emission maxima range from yellow (**18b**,  $\lambda_{em} = 588$  nm), orange (**18a** and **18c**) to red/deep-red (**19b**, **20b**, **20c**, **19a**, **19c**, **20a**, **21b**) and even near-infrared ( $\lambda_{em} > 750$  nm for **21a** and **21c**) depending on the donor-group or length of the  $\pi$ -conjugated bridge. Consistent with what was observed with 2-oxo-2,5-dihydrofuran derivatives, 9-ethyl-9*H*-carbazolyl- based compounds **18a-c** display only a very weak emission.<sup>7b</sup> The same applies to compound **19a** incorporating a *phenylsulfonyl* group and the 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)- electron donor group. On the other hand, an intense emission is observed for the 2-(7-*N,N*-diphenylamino)-9,9-diethylfluorenyl-derivatives **21a-21c**, with remarkable quantum yield values of 13 % (**21c**), 30 % (**21a**) and 37 % (**21b**) measured for emission maxima in the far-red/NIR range at 790 nm, 718 nm and 788 nm respectively.

As expected for push-pull dipolar dyes, all emissions are characterized by large Stokes' shifts (up to 6560  $\text{cm}^{-1}$  for **19b**) and a pronounced positive solvatochromism, except for compound **18c**. The solvatochromism properties of compounds **20b** and **21b** are shown as examples in Figure 5, while the data for all compounds are given in Figures SI-11-46. These positive solvatochromic properties can be analyzed according to the Lippert-Mataga model introducing the solvent polarity parameter  $\Delta f$ . For all compound with the exception of **18c**, good linear correlations are found when the Stokes' shift  $\Delta \bar{\nu}$ , expressed in  $\text{cm}^{-1}$ , is plotted against  $\Delta f$  with very large slope values  $s$  ranging from  $s = 4591\text{-}7200$   $\text{cm}^{-1}$  for **18a** and **18b** to  $s = 7200\text{-}7900$   $\text{cm}^{-1}$  for series **20**,  $s = 10800\text{-}13680$   $\text{cm}^{-1}$  for series **21** to  $s = 12326\text{-}16093$   $\text{cm}^{-1}$  for compounds **19**. This is far more than Prodan, a reference solvatochromic dye ( $s = 6347$   $\text{cm}^{-1}$ ),<sup>22</sup> and compares directly with superior solvatochromic push-pull fluorophores composed of a fluorene aromatic core or a diazaborine as  $\pi$ -conjugated bridge.<sup>23</sup> The Lippert-Mataga slope directly correlates to the dipole moment change  $\Delta\mu = \mu_e - \mu_g$ , and such large slope could likely be ascribed to an increase of the charge transfer due to an enhancement in the excited state dipole moment.<sup>23b</sup>



**Figure 4.** Normalized absorption (dashed) and emission (continuous) spectra of **21a-21c** in  $\text{CHCl}_3$ . For the emission measurements, excitation was at the maximum absorption wavelength.



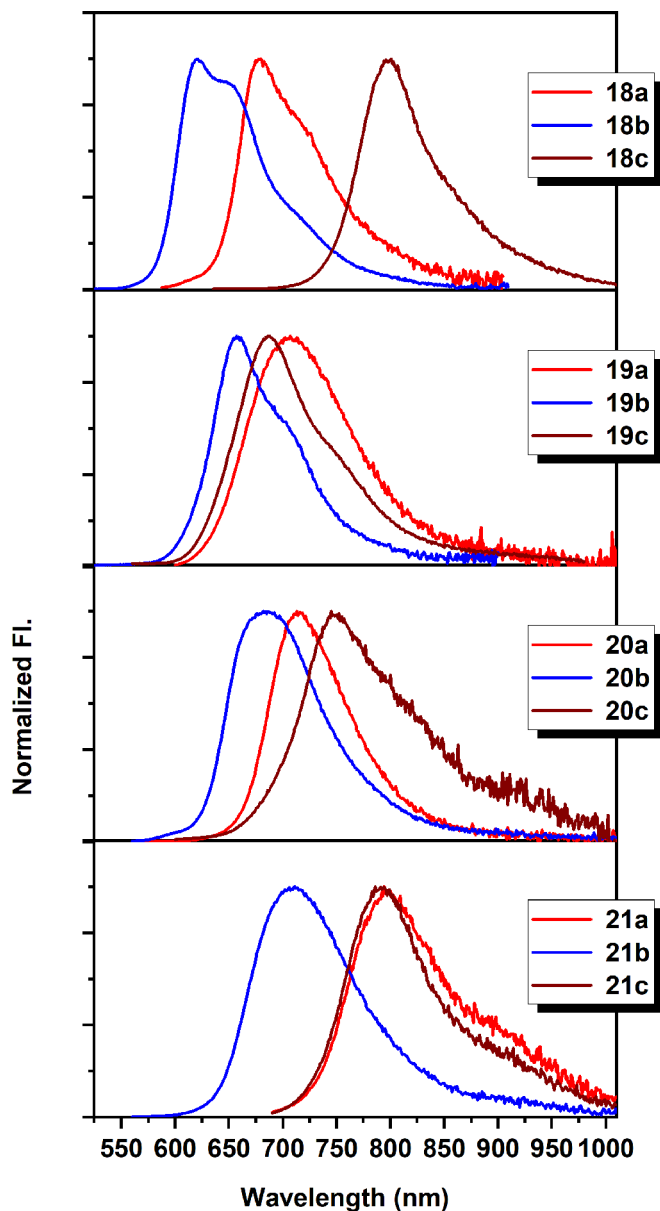
**Figure 5.** Normalized absorption in cyclohexane (dashed) and emission in various solvents (continuous) for **20b** and **21b**. For the emission measurements, **20b** was excited at 475 nm and **21b** was excited at 490 nm. Note that the emission in dimethylsulfoxide for **21b** is too weak and was discarded for the figure.

**Table 2.** Spectroscopic properties for all compounds **18-21** in solution in  $\text{CHCl}_3$  and in solid

	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) [a]	$\lambda_{\text{max}}$ (nm) [a]	$\lambda_{\text{em}}$ (nm) [a]	$\Phi_{\text{f}}$ (%) [a,b]	$\lambda_{\text{em}}$ (nm) [a]	$\Phi_{\text{s}}$ (%) [c,d]
<b>18a</b>	12 700	506	601	1 <sup>b</sup>	664	9
<b>18b</b>	32 700	468	588	1 <sup>b</sup>	606	24
<b>18c</b>	24 000	514	608	1 <sup>e</sup>	789 <sup>e</sup>	4 [e]
<b>19a</b>	28 200	515	725	< 0.1	710	8
<b>19b</b>	17 200	463	665	10 <sup>b</sup>	658	29
<b>19c</b>	26 300	523	720	3	688	3
<b>20a</b>	49 700	566	717	12 <sup>c</sup>	713	3
<b>20b</b>	18 400	503	645	7 <sup>b</sup>	685	15
<b>20c</b>	42 000	572	711	8 <sup>e</sup>	750 <sup>e</sup>	< 1 [e]
<b>21a</b>	41 600	570	788	30 <sup>d</sup>	800	9
<b>21b</b>	36 600	509	718	37 <sup>b</sup>	710	28

[a] In solution in CHCl<sub>3</sub>; [b] In solution in CHCl<sub>3</sub> using Rubrene ( $\Phi_f = 27\%$  in MeOH)<sup>24</sup>, Cresyl violet ( $\Phi_f = 54\%$  in MeOH)<sup>24</sup> or Styryl 9M ( $\Phi_f = 54\%$  in CHCl<sub>3</sub>)<sup>25</sup> as references; [c] In solid (powder); [d] measured using a calibrated integrating sphere (model GMP G8). [e] From reference <sup>7b</sup>.

Additionally, the emission quantum yields are also very much solvent dependent, generally increasing with solvent polarity from cyclohexane to chloroform, but then strongly decreasing when still increasing the polarity. Only exceptions are compounds **18a-c** for which a continuous, albeit moderate, increase of the quantum yield values with an increase of solvent polarity was observed (Table SI-6). It is worth noting that, with the notable exception of the 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-series, the *phenylthio* and *phenylsulfonyl* compounds are brighter than the *cyano* analogues, especially for the series **21** with 64 % quantum yield at 713 nm measured in toluene for **21a** against 26 % ( $\lambda_{em} = 724$  nm) for **21c**.



**Figure 6.** Emission spectra of compounds **18-21** in the solid state.

All these fluorophores were found to be emissive in the solid state. Measurements (emission spectra and quantum yield) were therefore performed on the crystalline powder using a calibrated integrating sphere. Figure 6 show all the emission spectra obtained while data are compiled in Table 2. The emission spectra are broad with emission maxima beyond 660 nm, except for **18b** (606 nm) and **19b** (658 nm), reaching 800 nm for **21a**. The maximum emission wavelength in solid is similar to the one obtained in a low-polarity solvent solution, except for the **18** series where a consequent red shift compared to the reddest shifted solution emission is observed, particularly for **18c**. The *phenylthio* compounds are by far the most emissive of all the series, whereas *phenylsulfonyl* compounds are usually more emissive than their *ciano* analogues further justifying the interest of these two new electron-acceptor

groups. These differences are all the more marked on the series **20** for which the *cyano*- derivative **20c** is hardly emissive ( $\Phi_s < 1\%$ ). More interestingly, the emission quantum yields are quite high for far-red/NIR emission up to  $\Phi_s = 29\%$  at 658 nm for **19b**,  $\Phi_s = 28\%$  at 710 nm for **21b** and still reaching  $\Phi_s = 9\%$  at 800 nm for **21a**, and may arise from the solid state structure described above.

## Conclusion

Two strong electron-accepting building blocks based on a 4,5,5-trimethyl-2,5-dihydrofuran scaffold have been developed and incorporated in various push-pull dipolar structures. The absorption spectra, luminescence properties at room temperature in solution and in the solid state have been investigated and compared with the *TCF* analogues. In general, dyes based on the novel acceptors **5** and **6** showed increased fluorescence QY in solution and in crystalline powder. The two most interesting compounds are **21a** and **21c** which presented a set of very promising solid state and solution fluorescence properties with emission maxima in the NIR spectral range and high quantum yield. Moreover, fluorophores presenting strong solvatochromism in the far-red to near-infrared are of particular interest for bio-imaging as recently proved by Klymchenko and co-workers with push-pull dioxaborine dyes exhibiting unprecedented red shift between liquid ordered and disordered membrane phases, allowing imaging of separated membrane microdomains and two-color imaging of polarity mapping in plasma membrane for monitoring the response of cells to stress.<sup>23c</sup> Additional studies on further synthetic manipulations of the furans and on the complete spectroscopic properties and on the practical use of the push-pull fluorophores reported here are ongoing in our laboratory.

## Experimental Section

**General information:** Chemical reagents and reagent grade solvents were used as received. Microwave syntheses were conducted in 20 mL or 5 mL sealed tube on a Biotage Initiator 2.5 single-mode reactor using external IR temperature control. Reaction monitoring was performed by analytical thin-layer chromatography (TLC) on Merck 60 F254 precoated silica gel plate (0.2 mm thickness) with visualization using a UV lamp. Purifications by column chromatography were carried out using 35-70  $\mu\text{m}$  silica gel. NMR spectra were recorded at ambient temperature on Bruker Advance 300, 400 or 500 operating at 300.1, 400.0 or 500.0 MHz for  $^1\text{H}$  and 75.0, 101.00 or 125.0 MHz for  $^{13}\text{C}$ , respectively. Chemical shifts are given in parts per million ( $\delta/\text{ppm}$ ) and are reported relative to tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) using the residual solvent peaks as internal standard.  $^1\text{H}$  NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets) or m (multiplets). Infrared spectra (IR) were recorded on a FT-IR spectrophotometer and are reported as wavenumber ( $\nu/\text{cm}^{-1}$ ). High resolution mass spectra (HRMS) were recorded at the Centre Commun de Spectrométrie de Masse (UCBL, Villeurbanne,

France) or at the Spectropole de St Jérôme (Univ Aix Marseille, France) using SYNAPT G2 HDMS (Waters) spectrophotometer. Compounds **11**,<sup>26</sup> **12**,<sup>27</sup> **15**,<sup>28</sup> **16**,<sup>20</sup> **17**,<sup>29</sup> **18c** and **20c**,<sup>7b</sup> and **TCF**<sup>30</sup> were synthesized according to previously reported methods.

#### **4,5,5-trimethyl-3-(benzo[d]thiazol-2-yl)-2(5H)-furanimine (8)**

In a 20 mL microwave vial equipped with a magnetic stirrer, a fresh solution of NaOEt in EtOH was prepared by adding Sodium (70 mg, 3 mmol) to dry EtOH (15 mL). After complete dissolution, 2-benzothiazoleacetonitrile **7** (1.57 g, 9 mmol) and 3-hydroxy-3-methyl-butan-2-one (0.92 g, 9 mmol) were added and the vial was sealed. The mixture was heated at 100°C by focused microwave irradiation under controlled temperature for 1 h. Solvent was then evaporated under vacuum and the product was purified by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/EtOH (98/2 v/v) to afford **8** as a brown oil (2.075 g, yield: 90 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.53 (s, 6H), 2.51 (s, 3H), 7.41 (dd, *J* = 8.2 Hz, *J* = 7.6 Hz, 1 H), 7.50 (dd, *J* = 7.95 Hz, *J* = 7.6 Hz, 1 H), 7.94 (d, *J* = 7.95 Hz, 1 H), 8.08 (d, *J* = 8.2 Hz, 1 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 13.1, 25.1, 88.5, 100.0, 120.3, 121.5, 123.3, 125.5, 126.3, 135.3, 152.9, 158.9, 164.6, 167.7 ppm; IR (neat): ν = 728, 758, 968, 1435, 1636, 1670, 1748, 2990 cm<sup>-1</sup>; HRMS (ESI-QTOF, pos): *m/z* calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>OS: 259.0900 [M+H]<sup>+</sup>; found: 259.0920.

#### **Synthesis of 9 and 10**

##### **Protocol 1**

In a microwave vial, to a solution of **8** (100 mg, 0.385 mmol, 1 equiv.), malononitrile (25 mg, 0.385 mmol, 1.0 equiv.) in dry MeOH (1 mL) was added pyrrolidine (one drop). Vial was then sealed and the mixture was heated at 80°C under focused microwaves for 1 h. After cooling down to RT, the solvent was evaporated under vacuum and the crude purified over a silica gel chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>. Yield: 65 mg of **9** (yellow solid, 54%) and 24 mg of **10** (white solid, 17%).

##### **Protocol 2**

In a microwave vial, to a solution of **8** (100 mg, 0.385 mmol, 1 equiv.), malononitrile (50 mg, 0.770 mmol, 2.0 equiv.) in dry MeOH (1 mL) was added pyrrolidine (one drop). Vial was then sealed and the mixture was heated at 80°C under focused microwaves for 1 h. After cooling down to RT, the solvent was evaporated under vacuum and the crude purified over a silica gel chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (100/0 to 96/4 v/v) affording a white solid, yield: 22 mg of **9** (yellow solid, 18%) and 105 mg of **10** (white solid, 73%).

#### **5-imino-2,2-dimethyl-1-methylene-2,5-dihydro-1H-benzo[4,5]thiazolo[3,2-a]furo[3,2-c]pyridine-4-carbonitrile (9)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.60 (s, 6H), 4.92 and 5.00 (ABq, <sup>2</sup>*J*<sub>AB</sub> = 1.98 Hz, 2 H), 7.37-7.43 (m, 1 H), 7.48-7.54 (m, 1 H), 7.62 (broad s, 1H), 7.63-7.68 (m, 1 H), 9.67 and 9.68 (s + s, 1 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 28.4, 75.0, 96.3, 100.2, 100.9, 114.9, 121.6, 124.9, 126.0, 127.6, 138.4, 146.4, 146.6, 158.2, 168.2 ppm; IR (neat): ν = 748, 1108, 1173, 1557, 1617, 2208 (ν<sub>C=N</sub>) cm<sup>-1</sup>; HRMS (ESI-QTOF, pos): *m/z* calcd for C<sub>17</sub>H<sub>14</sub>N<sub>3</sub>OS: 308.0852 [M+H]<sup>+</sup>; found: 308.0846.

#### **2-(1-amino-2-cyano-3-oxo-3H-benzo[4,5]thiazolo[3,2-a]pyridin-4-yl)-2,3,3-trimethylcyclopropane-1,1-dicarbonitrile (10)**

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 1.30 (s, 3 H), 1.42 (s, 3 H), 1.49 (s, 3 H), 7.44-7.58 (m, 2 H), 7.78 (s, 2 H), 8.09 (dd, <sup>3</sup>*J* = 8.1Hz, <sup>4</sup>*J* = 1.2Hz, 1 H), 8.21 (d, <sup>3</sup>*J* = 8.1Hz, 1 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO): δ = 14.9, 18.0, 19.0, 21.4, 41.2, 42.7, 83.5, 112.8, 113.8, 114.1, 115.8, 117.5, 123.6, 125.0, 126.5, 126.7, 136.5, 150.7, 155.4, 170.9 ppm; IR (neat): ν = 752, 1448, 1490, 1592, 2213 (ν<sub>C=N</sub>) cm<sup>-1</sup>; HRMS (ESI-QTOF, pos): *m/z* calcd for C<sub>20</sub>H<sub>15</sub>N<sub>5</sub>OSNa: 396.0890 [M+Na]<sup>+</sup>; found: 396.0873.

#### **4,5,5-trimethyl-3-(phenylthio)-2(5H)-furanimine (13)**

In a 20 mL microwave vial equipped with a magnetic stirrer, a fresh solution of NaOEt in EtOH was prepared by adding Sodium (100 mg, 4.3 mmol) to dry EtOH (5 mL). Once all the Sodium was consumed, **12** (3.2 g, 21.4 mmol) and 3-hydroxy-3-methylbutan-2-one (2.2 g, 21.5 mmol) were added and the vial was sealed. The mixture was heated to 55°C for 30 minutes by focused microwave irradiation under controlled temperature. After cooling back to RT, CH<sub>2</sub>Cl<sub>2</sub> was added and the residual sodium salts were filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the crude purified over a short silica gel chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/EtOH (100/0 to 96/4 v/v) to afford the title product (4.45g, 95 % yield) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.49 (s, 6 H), 2.06 (s, 3 H), 7.18-7.22 (m, 3 H), 7.26-7.30 (m, 2 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 12.9, 25.5, 89.0, 119.9, 126.9, 128.2, 129.8, 134.6, 169.4 ppm; HRMS (ESI-QTOF, pos): m/z calcd for C<sub>13</sub>H<sub>16</sub>NOS: 234.0947 [M+H]<sup>+</sup>; found: 234.0947.

#### **2-(3-phenylthio-4,5,5-trimethyl-2(5H)-furanilidene)-propanedinitrile (6)**

In a 20 mL microwave vial equipped with a magnetic stirrer, a fresh solution of NaOEt in EtOH was prepared by adding Sodium (100 mg, 4.3 mmol) to dry EtOH (5 mL). Once all the Sodium was consumed, **13** (0.95 g, 4.1 mmol) and malononitrile (540 mg, 8.2 mmol) were added and the vial was sealed. The mixture was heated to 100°C by focused microwave irradiation under controlled temperature for 1 h. Additional malononitrile (270 mg, 4.1 mmol) was added and the mixture was heated by focused microwave irradiation for more 1 h, at which point <sup>1</sup>H-NMR indicated that the imino-lactone **12** has been completely consumed. After cooling down to RT, the solvent was evaporated. The residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and water. The layers were separated. The organic layer was washed twice more with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. Purification by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> afforded pure **6** as off-white solid (0.97 g, 84 %, yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.61 (s, 6 H), 2.21 (s, 3 H), 7.21-7.15 (m, 2 H), 7.23-7.28 (m, 1 H), 7.31-7.38 (m, 2 H), ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 13.7, 25.1, 57.0, 98.4, 112.6, 113.6, 121.0, 127.5, 128.1, 130.1, 134.1, 178.6, 182.0 ppm; IR (neat): ν = 728, 1312, 1381, 1479, 1558, 2211 (ν<sub>C=N</sub>), 2224 (ν<sub>C=N</sub>), 2983 cm<sup>-1</sup>; HRMS (ESI-QTOF, neg): m/z calcd for C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>OS: 281.0754 [M+H]<sup>-</sup>; found: 281.0744.

#### **2-(3-phenylsulfonyl-4,5,5-trimethyl-2(5H)-furanilidene)-propanedinitrile (5)**

**6** (500 mg, 1.77 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). mCPBA (1.5 g, 4.8 mmol, 2.7 equiv.) was added and the reaction was heated at 35 °C for 60 h until complete formation of the sulfone as indicated by <sup>1</sup>H-NMR. The solvent was then evaporated and the crude recrystallized from Pentane/EtOH to afford pure **5** as a white solid (500 mg, 90 % yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.59 (s, 6 H), 2.58 (s, 3 H), 7.62-7.66 (m, 2 H), 7.72-7.76 (m, 1 H), 7.97-7.99 (m, 2 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 14.5, 24.7, 59.8, 97.9, 112.6, 113.3, 128.1, 129.4, 130.3, 135.3, 140.0, 175.0, 181.0 ppm; IR (neat): ν = 1155, 1392, 1445, 1577, 1586, 2222 (ν<sub>C=N</sub>), 2995 cm<sup>-1</sup>; HR-MS (ESI-QTOF, pos): m/z calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>SNa: 337.0617 [M+Na]<sup>+</sup>; found: 337.0614.

#### **General procedure for the synthesis of dyes 18a/c-21a/c**

In a 20 mL microwave vial equipped with a magnetic stirrer, acceptor compound **5** or **6** or *TCF* (1 equiv.) and aldehyde **14-17** (1.1 equiv.) were dissolved in absolute EtOH (5 mL for 0.30 mmol). Piperidine (one drop) was added and the vial was sealed. The solution was heated at 100°C using focused microwave irradiation under controlled temperature for 30 min to 1 h. It was then let cool down to RT at which point the dye precipitated. It was filtered, washed with cold ethanol. If needed, the precipitate was recrystallized in absolute ethanol to give the final product.

### **2-[3-phenylsulfonyl-4-[(1E)-2-(9-ethyl-9H-carbazol-3-yl)ethenyl]-5,5-dimethyl-2(5H)-furanlidene]-propanedinitrile (18a)**

Obtained from **5** (100 mg, 0.32 mmol.) and **14** (78 mg, 0.35 mmol.), heating 40 min. Filtration and recrystallization from absolute EtOH gave **18a** as a dark red solid (55 mg, 33 % yield). Mp: 239-240°C;

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.47 (t, <sup>3</sup>J = 7.3 Hz, 3 H), 1.90 (s, 6 H), 4.43 (q, <sup>3</sup>J = 7.3 Hz, 2 H), 7.30-7.36 (m, 1 H), 7.47-7.77 (m, 7 H), 7.91 (dd, <sup>3</sup>J = 8.7 Hz, <sup>4</sup>J = 1.4 Hz, 1 H), 8.02-8.09 (m, 2 H), 8.17 (d, <sup>3</sup>J = 7.8 Hz, 1 H), 8.42 (s, 1 H), 8.44 (d, <sup>3</sup>J<sub>trans</sub> = 18.0 Hz, 1 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 14.2, 28.2, 38.6, 57.8, 95.3, 110.0, 110.4, 122.9, 113.6, 114.4, 121.0, 121.2, 123.0, 123.2, 124.1, 124.4, 126.5, 127.3, 127.5, 127.8, 130.1, 134.8, 141.0, 141.3, 143.3, 150.5, 172.4, 174.8 ppm; HRMS (ESI-QTOF): m/z calcd for C<sub>31</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>SNa: 542.1509 [M+Na]<sup>+</sup>; found: 542.1498.

### **2-[4-[(1E)-2-[4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl]ethenyl]-3-phenylsulfonyl-5,5-dimethyl-2(5H)-furanlidene]-propanedinitrile (19a)**

Obtained from **5** (100 mg, 0.32 mmol.) and **15** (135 mg, 0.35 mmol.), 40 min heating. Filtration gave **19a** as a dark red powder (135 mg, 62 % yield). Mp: > 260°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.46 (s, 18 H), 1.90 (s, 6 H), 7.45–7.57 (m, 5 H), 7.62-7.67 (m, 2 H), 7.71-7.79 (m, 3 H), 7.94 (d, <sup>3</sup>J = 8.5 Hz, 2 H), 8.01-8.08 (m, 2 H), 8.16 (m, 2 H), 8.48 (d, <sup>3</sup>J<sub>trans</sub> = 16.7 Hz, 1 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 28.1, 32.2, 35.2, 59.6, 95.6, 109.9, 113.2, 113.9, 116.4, 117.1, 124.5, 124.6, 126.2, 127.1, 128.0, 130.3, 131.2, 133.2, 135.1, 138.9, 140.5, 142.5, 144.6, 146.9, 171.5, 174.5 ppm; HRMS (ESI-QTOF, neg): m/z calcd for C<sub>43</sub>H<sub>40</sub>N<sub>3</sub>O<sub>3</sub>S: 678.2796 [M-H]<sup>-</sup>; found: 678.2770.

### **2-[3-phenylsulfonyl-4-[2-[4-(diphenylamino)phenyl]ethenyl]-5,5-dimethyl-2(5H)-furanlidene]propanedinitrile (20a)**

Obtained from **5** (100 mg, 0.32 mmol.) and **16** (96 mg, 0.35 mmol), 40 min heating. Filtration afforded **20a** as a green powder (135 mg, 75 % yield). Mp: 169-170°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.82 (s, 6H), 7.00 (d, <sup>3</sup>J = 8.9 Hz, 2 H), 7.10-7.29 (m, 6 H), 7.28-7.41 (m, 5 H), 7.52-7.55 (m, 2H), 7.58-7.60 (m, 2H), 7.67-7.72 (m, 1H), 8.03-7.93 (m, 2H), 8.19 (d, <sup>3</sup>J<sub>trans</sub> = 16.5 Hz, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 28.2, 57.7, 95.1, 112.7, 113.6, 114.4, 120.4, 123.0, 126.0, 126.9, 127.4, 127.8, 130.1, 130.3, 131.6, 134.7, 141.0, 146.4, 148.4, 152.8, 172.1, 174.8 ppm; HRMS (ESI-QTOF, pos): m/z calcd for C<sub>35</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>SNa: 592.1665 [M+Na]<sup>+</sup>; found: 592.1653.

### **2-[3-phenylsulfonyl-4-[2-[7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl]-ethenyl]-5,5-dimethyl-2(5H)-furanlidene]propanedinitrile (21a)**

Obtained from **5** (100 mg, 0.32 mmol.) and **17** (146 mg, 0.35 mmol), 40 min heating. Filtration and recrystallization from absolute EtOH gave **21a** as a black powder (125 mg, 55 % yield). Mp: 235-326°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 0.36 (t, <sup>3</sup>J = 7.3 Hz,

6 H), 1.88 (s, 6 H), 1.97-1.90 (m, 2 H), 2.06-1.97 (m, 2 H), 7.02-7.14 (m, 8 H), 7.29-7.32 (m, 4 H), 7.51 (d,  $^3J_{\text{trans}} = 16.6$  Hz, 2 H), 7.61-7.73 (m, 7 H), 8.03 (d,  $J = 8$  Hz, 2 H), 8.39 (d,  $J = 16.6$  Hz, 1 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.8, 28.1, 33.0, 56.7, 58.6, 95.4, 113.4, 114.2, 114.6, 118.4, 120.3, 122.1, 123.2, 123.8, 124.3, 124.5, 125.1, 127.8, 129.5, 129.9, 130.2, 133.2, 134.9, 135.0, 140.7, 147.2, 148.1, 149.3, 149.6, 151.5, 153.2, 171.9, 174.6$  ppm; HRMS (EI-QTOF, pos):  $m/z$  calcd for  $\text{C}_{46}\text{H}_{39}\text{N}_3\text{O}_3\text{SNa}$ : 736.2604  $[\text{M}+\text{Na}]^+$ ; found 736.2589.

### **2-[3-phenylthio-4-[(1E)-2-(9-ethyl-9H-carbazol-3-yl)ethenyl]-5,5-dimethyl-2(5H)-furanlydene]-propanedinitrile (18b)**

Obtained from **6** (100 mg, 0.35 mmol.) and **14** (87 mg, 0.39 mmol.), heating 30 min Filtration and recrystallization from absolute EtOH afforded **18b** as orange solid (115 mg, 67 % yield). Mp: 245-246°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 1.44$  (t,  $^3J = 7.2$  Hz, 3 H), 1.90 (s, 6 H), 4.39 (q,  $^3J = 7.2$  Hz, 2 H), 7.24-7.37 (m, 6 H), 7.42-7.53 (m, 4 H), 7.57 (d,  $^3J_{\text{trans}} = 16.7$  Hz, 1 H), 7.75 (dd,  $^3J = 8.6$  Hz,  $^4J = 1.4$  Hz, 1 H), 8.13 (d,  $^3J = 7.8$  Hz, 1 H), 8.32 (d,  $^4J = 1.4$  Hz, 1 H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 14.2, 27.4, 38.5, 55.8, 96.6, 109.8, 109.9, 113.4, 114.4, 114.5, 118.0, 120.6, 121.1, 122.1, 123.2, 124.2, 126.6, 126.7, 127.2, 127.4, 128.0, 130.1, 135.1, 141.2, 142.4, 145.2, 172.3, 181.4$  ppm; HRMS (ESI-QTOF, neg):  $m/z$  calcd for  $\text{C}_{31}\text{H}_{25}\text{N}_3\text{OSCl}$ : 522.1412  $[\text{M}+\text{Cl}]^-$ ; found: 522.1432.

### **2-[4-[(1E)-2-[4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl]ethenyl]-3-phenylthio-5,5-dimethyl-2(5H)-furanlydene]-propanedinitrile (19b)**

Obtained from **6** (100 mg, 0.35 mmol.) and **15** (150 mg, 0.39 mmol.), 30 min heating. Filtration and recrystallization from absolute ethanol gave **19b** as a red powder (175 mg, 77 % yield). Mp: 256-258°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 1.45$  (s, 18 H), 1.89 (s, 6 H), 7.20-7.31 (m, 3 H), 7.41-7.55 (m, 8 H), 7.68 (d,  $^3J_{\text{AB}} = 8.5$  Hz, 2 H) 7.82 (d,  $^3J_{\text{AB}} = 8.5$  Hz, 2 H), 8.15 (d,  $^4J = 1.5$  Hz, 2H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 27.3, 32.2, 35.2, 57.2, 96.8, 109.8, 113.0, 114.0, 117.0, 117.9, 120.9, 124.3, 124.4, 127.1, 127.7, 128.2, 130.1, 130.2, 133.8, 134.6, 139.1, 141.2, 142.2, 144.3, 171.1, 181.1$  ppm; HRMS (ESI-QTOF, neg):  $m/z$  calcd for  $\text{C}_{43}\text{H}_{40}\text{N}_3\text{OS}$ : 646.2898  $[\text{M}-\text{H}]^-$ ; found: 646.2881.

### **2-[3-phenylthio-4-[2-[4-(diphenylamino)phenyl]ethenyl]-5,5-dimethyl-2(5H)-furanlydene]propanedinitrile (20b)**

Obtained from **6** (150 mg, 0.53 mmol.) and **16** (158 mg, 0.58 mmol), 1 h heating. Filtration and recrystallization from absolute EtOH gave **20b** as a red powder (190 mg, 66 % yield). Mp: 239-240°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 1.82$  (s, 6 H), 6.97 (d,  $^3J = 8.9$  Hz, 2 H), 7.10-7.27 (m, 11 H), 7.28-7.32 (m, 6 H), 7.41 (d,  $^3J = 8.9$  Hz, 2 H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 27.3, 55.8, 96.5, 113.4, 114.4, 114.6, 118.2, 121.2, 125.3, 126.5, 127.4, 127.9, 128.2, 130.0, 130.1, 130.2, 135.0, 143.3, 146.9, 151.4, 172.0, 181.3$  ppm; HRMS (ESI-QTOF, neg):  $m/z$  calcd for  $\text{C}_{35}\text{H}_{27}\text{N}_3\text{OSCl}$ : 572.1569  $[\text{M}+\text{Cl}]^-$ ; found: 572.1553.

### **2-[3-phenylthio-4-[2-[7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl]-ethenyl]-5,5-dimethyl-2(5H)-furanlydene]propanedinitrile (21b)**

Obtained from **6** (80 mg, 0.28 mmol.) and **17** (130 mg, 0.31 mmol), 40 min heating. Filtration and recrystallization from absolute EtOH gave **21b** as a dark red powder (120 mg, 63 % yield). Mp: 252-253°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 0.32$  (t,  $^3J = 7.3$  Hz, 6 H), 1.87 (s, 6 H), 1.88-2.01 (m, 4 H), 6.93-7.14 (m, 8 H), 7.18-7.50 (m, 12 H), 7.55-7.66 (m, 3 H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (101

MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.8, 27.4, 33.0, 56.4, 56.8, 96.7, 113.3, 114.2, 116.2, 118.8, 119.4, 120.0, 121.7, 122.8, 123.5, 123.6, 124.9, 127.5, 128.1, 128.8, 129.8, 130.1, 133.6, 134.9, 135.5, 144.2, 145.7, 148.3, 149.1, 151.3, 152.8, 171.5, 181.2 ppm; HRMS (ESI-QTOF, neg): m/z calcd for C<sub>46</sub>H<sub>39</sub>N<sub>3</sub>OSCl: 716.2508 [M+Cl]<sup>-</sup>; found: 716.2488.

**2-[4-[(1E)-2-[4-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)phenyl]ethenyl]-3-cyano-5,5-dimethyl-2(5H)-furanylidene]-propanedinitrile (19c)**

Obtained from **TCF** (50 mg, 0.25 mmol.) and **15** (95 mg, 0.25 mmol), 30 min heating. As the final compound did not precipitate, the solvent was evaporated to dryness and the crude taken in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and purified by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>. followed by recrystallization from absolute ethanol. **19c** was obtained as a red powder (55 mg, 39 % yield). Mp > 260°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.50 (s, 18 H), 1.87 (s, 6H), 7.12 (d, <sup>3</sup>J<sub>trans</sub> = 16.1 Hz, 1H), 7.48 (d, <sup>3</sup>J<sub>AB</sub> = 8.8 Hz, 2H), 7.52 (dd, <sup>3</sup>J<sub>AB</sub> = 8.8 Hz, <sup>4</sup>J<sub>meta</sub> = 1.4 Hz, 2H), 7.78 (d, <sup>3</sup>J<sub>trans</sub> = 16.1 Hz, 1H), 7.78 (d, <sup>3</sup>J<sub>AB</sub> = 8.3 Hz, 2H), 7.90 (d, <sup>3</sup>J<sub>AB</sub> = 8.3 Hz, 2H), 8.16 (d, <sup>4</sup>J<sub>meta</sub> = 1.4 Hz, 2H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 26.7, 32.1, 34.9, 97.8, 100.2, 109.4, 110.4, 110.9, 111.7, 114.9, 116.7, 124.1, 124.3, 126.7, 130.8, 131.6, 138.4, 142.7, 144.3, 146.3, 173.6, 175.3 ppm; HRMS (ESI-QTOF): m/z calcd for C<sub>38</sub>H<sub>37</sub>N<sub>4</sub>O [M+H]<sup>+</sup>, 565.2962; found, 565.2947.

**2-[3-cyano-4-[2-[7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl]-ethenyl]-5,5-dimethyl-2(5H)-furanylidene]propanedinitrile (21c)**

Obtained from **TCF** (100 mg, 0.53 mmol.) and **17** (200 mg, 0.48 mmol.), 1 h heating. Filtration and recrystallization from absolute ethanol gave **21c** as a violet crystalline solid (250 mg, 85 % yield). Mp > 260°C; <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  = 0.27 (t, <sup>3</sup>J = 6.9 Hz, 6 H), 1.82 (s, 6H), 1.87-1.93 (m, 2 H), 2.00-2.06 (m, 2 H), 6.96 (d, <sup>3</sup>J = 7.9 Hz, 1 H), 7.05-7.09 (m, 7 H), 7.26-7.34 (m, 5 H), 7.81-7.90 (m, 3 H), 8.00-8.02 (m, 2 H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  = 8.5, 25.3, 31.6, 53.8, 55.8, 97.9, 99.2, 111.1, 112.0, 112.9, 114.1, 117.9, 119.9, 122.2, 122.7, 123.3, 123.5, 123.9, 129.6, 130.2, 132.7, 134.6, 145.4, 147.1, 148.2, 148.4, 150.4, 152.2, 175.4, 177.2 ppm; HRMS (ESI-QTOF): m/z calcd for C<sub>41</sub>H<sub>34</sub>N<sub>4</sub>ONa [M+Na]<sup>+</sup>, 621.2625; found, 621.2628.

## Supporting Information

- X-ray crystallographic data for compound **6**, **9**, **10**, **20a**, **21a**, **20b** and **20b** (CIF).
- <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compounds **8**, **9**, **10**, **12**, **13**, **6**, **5**, **18a**, **19a**, **20a**, **21a**, **18b**, **19b**, **20b**, **21b**, **18c**, **19c**, **20c**, **21c**; scheme for the preparation of **9** and **10**; additional figures and data for spectroscopy, solvatochromism and Lippert-Matga analysis (PDF).

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