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# Synthesis, characterization and properties of novel bis(aryl)carbazole-containing *N*-coumarin derivatives

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ABSTRACT

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Keywords: N-coumarin Bis(aryl)carbazole Fluorescence Non-doped emitter Organic light-emitting diode A series of novel *N*-coumarin derivatives containing oligothiophene-substituted *N*-coumarins as the core and bis(aryl)carbazoles as the substituent were synthesized and characterized. Their optical, electrochemical and thermal properties were investigated. The electroluminescence (EL) properties of the selected materials were also studied. Solution-processed OLEDs with green and yellow light emission, turn-on voltages of 2.7-2.9 V and maximum luminance efficiencies of up to 3.94 cd A<sup>-1</sup> at 17.6 mA cm<sup>-2</sup> (maximum power efficiency of 1.62 lm W<sup>-1</sup>) were prepared.

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The discovery and development of new organic emitting materials (EMs) has played a major role in organic light-emitting diode (OLED) research.<sup>1</sup> The advance of OLEDs holds great promise for the next-generation lighting and flat panel display technology, with the advantage that they can be more economical to use and can exhibit electroluminescence at relatively low voltages, making them exceptionally useful for application in electronic devices.<sup>2</sup> It is desirable that EMs used in OLEDs have good morphological properties including a good film-forming ability, an amorphous or noncrystalline solid state, solution processability and good thermal stability characterized by high decomposition temperatures. Dendritic-like materials were an alternative class of amorphous molecular EMs for OLEDs.<sup>3</sup> They can be designed to possess conjugated cores for efficient emission and/or charge transport and appropriate terminal groups/chains for good processability.<sup>4</sup> So far, many types of fluorescent and phosphorescent EMs with dendritic-like structures have been developed.<sup>5</sup>

Coumarin and its derivatives are of significant interest because they are used extensively as laser dyes, fluorescent probes, optical brighteners and light absorbers for solar cells.<sup>6</sup> Generally, coumarin does not fluoresce, whereas its derivatives substituted at the 7-position with electron-donating groups [amino (*N*-coumarin) or hydroxyl (*O*-coumarin) groups] are highly fluorescent in the blue-green region. However, reports on

the use of coumarin derivatives as EL materials in OLEDs are rare due to the fact that they easily undergo self-quenching in the solid state due to interactions and aggregation with neighboring molecules.<sup>7</sup> Thus, as EL materials, the host materials are always doped at appropriate concentrations to fabricate OLEDs with reasonable luminescence efficiencies.<sup>8</sup>

In this Letter, we describe the preparation of new *N*-coumarin derivatives (Scheme 1). Our design involves the use of oligothiophene-substituted *N*-coumarins as the fluorescent core and a 3,6-bis(aryl)carbazole dendron as the substituent. The latter can suppress the aggregation-caused emission quenching of the highly fluorescent coumarin core as well as increase the hole-transporting ability, thermal stability and solubility of the molecule. Substitution of *N*-coumarin with oligothiophenes allows fine-tuning of the emission color. Herein, we report a detailed synthesis, and the physical and photophysical properties of these *N*-coumarins.

Scheme 1 outlines the synthesis of the target *N*-coumarin derivatives, **CTnR** (n = 1-2). They can be constructed by coupling of the *N*-coumarin intermediates **3** and **5** with each of 3,6-bis(aryl)carbazoles **6-9**. The bromide intermediate **3** was first prepared by condensation of the aldehyde **1** with thiophene-2-ylacetonitrile in the presence of piperidine as the base followed by bromination of the resulting thiophene **2** with NBS in THF. Suzuki cross-coupling of **3** with thiophene-2-boronic acid

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#### Tetrahedron Letters

catalyzed by  $Pd(PPh_3)_4/Na_2CO_3$  (aq) in THF and subsequent bromination of the product **4** with NBS afforded the corresponding bromide intermediate **5** in quantitative yield. The carbazoles **6-9** were prepared in good yields by the double Suzuki cross-coupling of 3,6-dibromocarbazole with the relevant aryl boronic acids under typical reaction conditions.<sup>9</sup> Finally, Ullmann coupling of the bromides **3** and **5** with each of the carbazole dendrons **6-9** catalyzed by CuI/K<sub>3</sub>PO<sub>4</sub>/(±)*trans*-1,2diaminocyclohexane in toluene gave the target *N*-coumarins, **CTnR** (n = 1-2) as yellow solids in moderate to good yields of 67-84%. All the prepared compounds were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and MALDI-TOF MS.<sup>10</sup> These *N*coumarins show high solubility in most organic solvents allowing thin films to be fabricated by a solution casting process.



Figure 1. The HOMO and LUMO orbitals calculated by the DFT/B3LYP/6-31G(d,p) method.

Quantum chemical calculations performed using the DFT/B3LYP/6-31G (d,p) method<sup>11</sup> reveal steric hindrance in the optimized structures of  $\mathbf{CTnR}$  (n = 1-2) (Figures 1 and S1). In all cases, the aryl-substituted carbazole wedges adopt twisted conformations relative to the plane of the oligothiophenesubstituted N-coumarin cores. Such structural characteristics can strongly influence optical and physical properties of the material such as the morphology and emission spectra.<sup>12</sup> In the LUMOs of all the molecules, the excited electrons are localized on the electron-deficient oligothiophene-substituted N-coumarin cores. Hence, molecules with the same N-coumarin cores (CT1R and **CT2R**) will have similar LUMO levels. It is also noticed that the electron delocalization length of the LUMOs of CT2R is longer than those of CT1R, which would lead to lower LUMO levels of CT2R compared to those of CTR. In the HOMOs of CTnPh and **CTnF**, the  $\pi$ -electrons are able to delocalize over the whole oligothiophene-substituted N-coumarin core and dendritic wedge through the lone electron pair of the N-atom of the carbazole, while in the HOMOs of **CTnTPA** and **CTnPYR**, the  $\pi$ -electrons delocalize only on the dendritic wedge.

The UV-Vis absorption spectra of CTnR feature two major peaks at 298-347 and 438-458 nm (Figure 2a, Table 1). The former corresponds to the n- $\pi^*$  transition of the aryl-substituted carbazole wedges, while the peak at longer wavelength is assigned to the  $\pi$ - $\pi^*$  electron transition in the oligothiophenesubstituted N-coumarin conjugated backbones. The  $\pi$ - $\pi$ \* transition peaks are red-shifted (~18 nm) to longer wavelengths with an increase in the number of thiophene units in the backbone due to the increased effective conjugation length, as expected. The positions of these peaks remain fairly constant throughout the series, where the  $\pi$ - $\pi$ \* transition peaks of **CTR** are observed at ~439 nm and those of CT2R are detected at ~457 nm. However, the absorptions of the dendritic wedges are varied depending on the extended conjugation system between the aryl groups and the carbazole which are in the order of pyrene (PYR)carbazole ( $\lambda = 347$  nm) > triphenylamine (TPA)-carbazole ( $\lambda =$ 337 nm) > fluorene (F)-carbazole ( $\lambda = 320$  nm) > tertbutylbenzene (Ph)-carbazole ( $\lambda = 298$  nm). The optical band gaps  $(E_{\sigma}^{opt})$  were calculated from the relevant absorption onsets to be ~2.41 eV and ~2.51 eV (Table 1). Upon photoexcitation, green

2

and yellow fluorescence was observed for CTR and CT2R, respectively. Their PL spectra show featureless emission bands, with the emission peaks centered around 511-520 nm and 529-533 nm, respectively (Figure 2b, Table 1). The PL spectra of CTR and CT2R are excitation wavelength independent, where, because of excitation either at the aryl-substituted carbazole wedges (298-347 nm) or N-coumarin cores (439-457 nm), the PL spectra obtained are identical. This implies that energy or excitons can efficiently transfer from the peripheral wedge to the emissive N-coumarin core. These compounds show small Stokes shifts (73-80 nm) indicating less energy loss during the relaxation process and efficient fluorescence. The fluorescence quantum yields ( $\Phi_{\rm F}$ ) of **CTR** and **CT2R** measured at room temperature in dilute CH<sub>2</sub>Cl<sub>2</sub> solution by comparing the PL intensity with that of a standard solution of quinine sulfate ( $\Phi_{\rm F} = 0.54$ ) are moderate, ranging from 0.35 to 0.64 (Table 1).



Figure 2. Plots of (a) absorption and (b) PL spectra in CH<sub>2</sub>Cl<sub>2</sub>.

Cyclic voltammetry (CV) analyses revealed that all the compounds underwent a single process of irreversible reduction at the cathodic potential  $(E_{pc})$  of ~1.7 V associated with the reduction of the electron-deficient N-coumarin moiety to form the anion radical (Figure 3a). The CTnTPA N-coumarins exhibit three quasi-reversible oxidation processes, while the remainder displayed two quasi-reversible oxidation processes. In all cases, the first oxidation peak corresponds to the removal of electrons from the peripheral triphenylamine (TPA) or carbazole group, resulting in radical cations. It is noted that the first oxidation of **CT2R**  $(E_{1/2}^{ox} = 0.73 \cdot 0.76 \text{ V})$  occurs at a lower potential than that of **CTR**  $(E_{1/2}^{ox} = 0.79 \cdot 0.84 \text{ V})$  (Table 1), in agreement with the longer effective conjugation length in CT2R than CTR, as observed in the optical properties. The radical cations formed from CTnTPA are electrochemically less stable than those of the other compounds in the series. This was confirmed by the presence of an additional peak at a lower potential on the cathodic scan ( $E_{pc}$ ) in the CV traces of **CTnTPA** ( $E_{pc} = 0.58$  and 0.63 V). Their repeated CV scans also display an increasing change in the CV traces, proving that a series of electrochemical reactions led to electro-polymerization of the radical cation species taking place on the glassy carbon electrode surface (Figure 3b). Usually, this type of electrochemical coupling reaction can be observed in most unsubstituted and less hindered TPA and carbazole derivatives.<sup>13</sup> However, this type of radicalradical coupling reaction will become inactive in a non-diffusion system or in the solid state. The multiple CV scans of **CTnPYR**, CTnPh and CTF showed identical CV curves with no extra peak on the cathodic scan, indicating no electrochemical oxidative coupling reaction of the radical cations formed (Figure 3c). The HOMO levels of these N-coumarins, estimated from CV and optical results, are in the range of -5.08 to -5.21 eV (Table 1), which are close to the work function of a commonly used indium tin oxide (ITO) anode (-4.80 eV). Their LUMO levels range from -2.67 eV to -2.80 eV, which are close to the work function of LiF/Al (-2.60 eV). From the CV, the energy gaps  $(E_g^{ele})$  are calculated to be in the range of 2.47-2.62 eV, which are close to the Eg opt values.



**Figure 3.** Plots of the CV traces measured in  $CH_2Cl_2$  in the presence of *n*-Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 50 mV s<sup>-1</sup>: (a) **CTR** and **CT2R**, (b) **CT2TPA** and (c) **CT2PYR**. (d) DSC (1<sup>st</sup> heating scan) and TGA traces measured under N<sub>2</sub>.

The differential scanning calorimetry (DSC) traces of the prepared samples displayed only an endothermic baseline shift related to the glass transition at temperatures (Tg) of 120-220 °C, and no exothermic crystallization or endothermic melting peaks were detected at higher temperatures (Figure 3d, Table 1). No crystallization was observed, indicating an excellent amorphous glass state stability. These results prove that integration of a bulky dendritic wedge in the molecule not only improved the thermal stability but also reduced the crystallization of the planar fluorescent N-coumarin core. Thermogravimetric analysis (TGA) revealed that the decomposition temperatures at 5% weight loss  $(T_{5d})$  are well over 400 °C, showing the excellent thermal stability. For optoelectronic applications, thermal stability of the organic materials is crucial for the device stability and lifetime.<sup>14</sup> Thermal instability or low T<sub>g</sub> of the amorphous organic layer shows that the device experiences faster degradation with increasing temperature or fails to function at a certain temperature above ambient. The cause of this instability is believed to be the morphological change near the T<sub>g</sub> in the amorphous organic layers used in the device.

The electroluminescence (EL) properties of several of these N-coumarins were investigated. The solution-processed doublelayer OLEDs [ITO/PEDOT:PSS/EML(spin-coating)(30-40 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm)] using CTTPA and CT2TPA as the emissive layers (EML) were fabricated and characterized (Figure S2 and Table S1). Under an applied voltage, the CTTPA- and CT2TPA-based devices exhibited green and yellow emission colors with featureless emission peaks  $(\lambda_{max}^{EL})$  at 536 and 552 nm, respectively. There was no emission shoulder detected at a longer wavelength caused by the excimer and exciplex species formed at the interface. The EL spectra of these OLEDs were identical with the solid film PL spectra of the EML, indicating that the light emissions were due solely to the emission of the EML. The operating voltages of these diodes at the turn-on voltage ( $V_{on}$ ) and 100 cd m<sup>-2</sup> ( $V_{100}$ ) were as low as 2.72-2.99 V and 4.50-5.30V, respectively. The CTTPA-based diode displays a maximum brightness ( $L_{max}$ ) of 7409 cd m<sup>-2</sup> at 13.0 V and shows a maximum luminous efficiency ( $\eta_{max}$ ) of 3.94 cd  $A^{-1}$  and a maximum power efficiency of 1.62 lm  $W^{-1}$ . The CT2TPA-based device displays a lower device performance with an  $L_{\text{max}}$  value of 4682 cd m<sup>-2</sup> and an  $\eta_{\text{max}}$  value of 2.10 cd A<sup>-1</sup> and a maximum power efficiency of 0.85 lm W<sup>-1</sup>. This may be due to the higher  $\Phi_F$  of **CTTPA**. It has been reported that the efficiency

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#### Tetrahedron Letters

of an OLED depends on both the balance of electrons and Table 1 Photophysical, physical and electrochemical data

holes, and on the  $\Phi_{\rm F}$  of the emitter.<sup>16</sup>

	·r,r	<b>J</b>						
Compound	$\lambda_{Abs}$	$\lambda_{\rm em}$	Stokes shift	$\Phi_{ m F}{}^{ m b}$	E <sub>1/2</sub> vs Ag/AgCl	$T_g/T_{5d}$	$E_g^{opt}/E_g^{ele}$	HOMO/LUMO
	$(nm)^{a}$	$(nm)^{a}$	(nm)		$(V)^{c}$	$(^{\circ}C)^{d}$	$(eV)^{e}$	$(eV)^e$
СТТРА	326, 440	520	80	0.55	-1.75 (E <sub>pc</sub> ), 0.63 (E <sub>pc</sub> ), 0.79,	150/432	2.51/2.58	-5.18/-2.67
					0.90, 1.16			
СТ2ТРА	337, 458	533	75	0.48	-1.72 (E <sub>pc</sub> ), 0.58 (E <sub>pc</sub> ), 0.73,	154/433	2.40/2.51	-5.08/-2.68
					0.90, 1.02			
CTPh	298, 439	515	76	0.52	-1.75 (E <sub>pc</sub> ), 0.84, 0.98	148/409	2.51/2.60	-5.21/-2.70
CT2Ph	297, 457	532	75	0.41	-1.69 (E <sub>pc</sub> ), 0.76, 0.89	161/423	2.41/2.48	-5.15/-2.74
CTPYR	346, 438	511	73	0.40	-1.75 (E <sub>pc</sub> ), 0.82, 0.91	196/423	2.52/2.61	-5.21/-2.69
CT2PYR	347, 455	529	74	0.35	-1.69 (E <sub>pc</sub> ), 0.73, 0.81	220/436	2.41/2.47	-5.21/-2.80
CTF	320, 439	517	78	0.64	-1.76 (E <sub>pc</sub> ), 0.82, 0.96	120/395	2.51/2.62	-5.18/-2.67
335	LL GTT GI							

Measured in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Measured in  $CH_2Cl_2$  with quinine sulfate as a standard ( $\Phi_F = 0.54$ ).<sup>15</sup>

<sup>c</sup> Analyzed by CV with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the electrolyte in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup> ( $E_{pc}$  = peak cathodic potential).

<sup>d</sup> Analyzed by DSC/TGA at a heat at e of 10 °C min<sup>-1</sup> under N<sub>2</sub>. <sup>e</sup> Calculated by  $E_g = 1240/\lambda^{abs}_{onset}$ ;  $E_g^{ele} = E_{pc}^{re} - E_{pa}^{ox}$  where  $E_{pc}$  is the peak cathodic potential and  $E_{pa}$  is the peak anodic potential; HOMO = -(4.44 +  $E^{ox}_{onset}$ ); LUMO = HOMO +  $E_g$ 

In summary, we have successfully synthesized and characterized of a series of new N-coumarins. By using arylsubstituted carbazole as the substituent, we were able to reduce the crystallization and retain the high emissive ability of the fluorescent coumarin cores as well as improve the amorphous stability. Preliminary studies show that they could be used as solution-processed non-doped emitters for OLEDs.

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#### **References and notes**

- (a) Kim, D. Y.; Cho, H. N.; Kim, C. Y. Prog. Polym. Sci., 2000, 25 1. 1089-1139. (b) Mitschke, U.; Bäuerle, P. J. Mater. Chem., 2000, 10, 1471-1507. (c) Khanasa, T.; Prachumrak, N.; Rattanawan, R.; Jungsuttiwong, S.; Keawin, T.; Sudyoadsuk, T.; Tuntulani, T.; Promarak, V. J. Org. Chem., 2013, 78, 6702-6713.
- (a) Kido, J.; Kimura, M.; Nagai, K. Science, 1995, 267, 1332-1334. (b) 2 Service, R. F. Science, 2005, 310, 1762-1763. (c) Eritt, M.; May, C.; Leo, K.; Toerker, M.; Radehaus, C. Thin Solid Films, 2010, 518, 3042-3045.
- (a) Li, J.; Liu, D. J. Mater. Chem., 2009, 19, 7584-7591. (b) Moonsin, 3. P.; Prachumrak, N.; Namuangruk, S.; Jungsuttiwong, S.; Keawin, T.; Sudyoadsuk, T.; Promarak, V. Chem. Commun., 2013, 49, 6388-6390.
- Lo, S. C.; Burn, P. L. Chem. Rev., 2007, 107, 1097-1116.
- 5. (a) Li, J.; Li, Q.; Liu, D. ACS Appl. Mater. Interfaces, 2011, 3, 2099-2107. (b) Moonsin, P.; Prachumrak, N.; Rattanawan, R.; Keawin, T.; Jungsuttiwong, S.; Sudyoadsuk, T.; Promarak, V. Chem. Commun., 2012, 48, 3382-3384. (c) Prachumrak, N.; Pojanasopa, S.; Namuangruk, S.; Kaewin, T.; Jungsuttiwong, S.; Sudyoadsuk, T.; Promarak, V. ACS Appl. Mater. Interfaces, 2013, 5, 8694-8703.
- (a) Kitamura, N.; Fukagawa, T.; Kohtani, S.; Kitoh, S. -I;. Kunimoto, K. -K.; Nakagaki, R.; J. Photochem. Photobiol. A, 2007, 188, 378-786. (b) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. Angew. Chem. Int. Ed., 1999, 38, 1422-1427. (c) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. Chem. Commun., 2001, 569-570.
- 7. (a) Yu, T.; Zhang, P.; Zhao, Y.; Zhang, H.; Meng, J.; Fan, D. Org. Electron., 2009, 10, 653-660. (b) Mitsuya, M.; Suzuki, T.; Koyama, T.; Shirai, H.; Taniguchi, Y. Appl. Phys. Lett., 2000, 77, 3272-3274.
- 8. (a) Yu, T.; Zhang, P.; Zhao, Y.; Zhang, H.; Meng, J.; Fan, D.; Chen, L.; Qiu, Y. Org. Electron., 2010, 11, 41-49. (b) Zhang, H.; Yu, T.; Zhao, Y.; Fan, D.; Xi, Y.; Zhang, P. Synth. Met., 2010, 160, 1642-1647.
- Li, H. Z.; Wong, M. S. Org. Lett., 2006, 8, 1499-1502.
- Characterization data for **CTPh**: m.p. 230-231 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 10. 3414, 2959, 1712, 1617, 1479, 1355, 1259, 1132, 807, 622; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.24 (6H, t, J = 3.9 Hz), 1.41 (18H, s), 3.44 (4H, q, J = 6.9 Hz), 6.57 (1H, d, J = 2.1 Hz), 6.62 (1H, dd, J = 8.7 Hz, J = 2.1 Hz), 7.22 (1H, d, J = 4.5 Hz), 7.35 (1H, d, J = 6.9 Hz), 7.51

(4H, d, J = 8.4 Hz), 7.62-7.75 (9H, m), 7.94 (1H, s), 8.35 (2H, d, J = 1.2 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 12.51, 31.44, 34.52, 44.92, 97.19, 108.70, 109.43, 110.74, 114.23, 118.55, 123.62, 124.22, 124.63, 125.76, 125.85, 126.98, 129.03, 134.15, 135.59, 136.83, 138.44, 138.95, 141.56, 149.65, 150.75, 155.68, 160.51; MALDI-TOF calcd for C49H48N2O2S: m/z 728.3436; found: m/z 728.4570 [M<sup>+</sup>]. CTTPA: m.p. 220-221 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3413, 2969, 1718, 1617, 1477, 1260, 1132, 696; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.25 (6H, t, J = 6.6 Hz), 3.44 (4H, bs), 6.58-6.64 (2H, m), 7.05-7.10 (4H, m), 7.20-7.34 (13H, m), 7.64-7.72 (8H, m), 7.91 (1H, s), 8.37 (2H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 12.42, 45.44, 109.39, 110.12, 110.79, 114.77, 118.25, 122.75, 123.82, 124.27, 124.39, 124.59, 125.58, 127.97, 128.88, 129.06, 129.24, 133.87, 135.43, 136.07, 136.61, 138.68, 141.45, 146.68, 147.84, 150.17, 155.56, 160.34; MALDI-TOF calcd for C<sub>65</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub>S: *m/z* 950.3654; found: *m/z* 950.4544 [M<sup>+</sup>] CTPYR: m.p. 244-245 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3415, 2952, 1710, 1617, 1528, 1480, 1264, 1134, 620; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.26 (6H, t, J = 6.7 Hz), 3.46 (4H, q, J = 6.9 Hz), 6.68 (1H, s), 6.78 (1H, d, J = 6.6 Hz), 7.39-7.43 (2H, m), 7.76 (2H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.4 Hz), 7.92-8.07 (4H, m), 8.10-8.20 (10H, m), 8.24 (2H, d, J = 7.8 Hz), 8.29 (2H, d, J = 9.3 Hz), 8.40 (2H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 12.30, 45.95, 110.46, 122.28, 123.88, 124.00, 124.64, 124.74, 124.91, 124.98, 125.05, 125.57, 125.95, 127.26, 127.47, 128.13, 128.86, 129.14, 129.37, 130.42, 131.06, 131.54, 134.05, 135.50, 136.50, 138.25, 138.84, 141.63, 155.43, 160.31; MALDI-TOF calcd for C<sub>61</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S: m/z 864.2810; found: m/z 864.4607 [M<sup>+</sup>]. CTF: m.p. 216-217 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3413, 2923, 1713, 1616, 1445, 1353, 1258, 1132, 623; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.82-0.94 (18H, m), 1.15-1.32 (44H, m), 2.11-2.14 (8H, m), 3.43 (4H, bs), 6.60-6.64 (2H, m), 7.28-7.45 (8H, m), 7.73-7.96 (14H, m), 8.54 (2H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 12.55, 14.16, 22.68, 23.92, 29.32, 29.79, 30.15, 31.87, 32.01, 40.56, 45.00, 55.27, 97.22, 108.78, 109.55, 110.90, 114.18, 118.84, 119.74, 120.04, 121.75, 122.96, 123.54, 124.36, 124.59, 126.23, 126.85, 126.95, 129.15, 134.95, 135.59, 136.84, 138.46, 139.95, 140.77, 141.00, 141.70, 150.71, 151.01, 151.58, 155.70, 160.61; MALDI-TOF calcd for C87H104N2O2S: m/z 1240.7819; found: m/z 1240.8121 [M<sup>+</sup>].

CT2Ph: m.p. 264-265 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3414, 2962, 1702, 1617, 1528, 1480, 1265, 1134, 620; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.25 (6H, bs), 1.40 (18H, s), 3.45 (4H, bs), 6.63 (1H, bs), 6.73 (1H, bs), 7.17 (1H, d, J = 3.9 Hz), 7.21 (1H, d, J = 3.6 Hz), 7.30 (1H, d, J = 3.6 Hz), 7.36 (1H, bs), 7.51 (4H, d, J = 8.4 Hz), 7.61-7.73 (9H, m), 7.93 (1H, s), 8.34 (2H, d, J = 0.9 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 12.35, 31.42, 34.52, 45.81, 98.39, 110.63, 118.60, 122.26, 124.18, 124.26, 125.44, 125.60, 125.76, 125.93, 126.98, 129.03, 134.34, 135.91, 136.03, 136.63, 137.21, 137.27, 138.87, 141.53, 149.72, 155.36, 160.25; MALDI-TOF calcd for C53H50N2O2S2: m/z 810.3314; found: m/z 810.6037 [M<sup>+</sup>].

CT2TPA: m.p. 239-240 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3414, 2972, 1702, 1617, 1478, 1273, 1132, 695; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.25 (6H, bs), 3.45 (4H, bs), 6.66 (1H, bs), 6.77 (1H, bs), 7.04 (4H, t, J = 7.2)Hz), 7.15-7.31 (24H, m), 7.37 (1H, d, J = 6.3 Hz), 7.59 (6H, d, J = 8.4 Hz), 7.68 (2H, dd, J = 11.7 Hz, J = 1.2 Hz), 7.94 (1H, s), 8.32 (2H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 12.35, 45.74, 110.68, 118.30,

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122.25, 122.78, 124.18, 124.28, 124.36, 125.39, 125.56, 125.65, 127.98, 129.01, 129.26, 134.01, 135.91, 135.97, 137.18, 141.43, 146.72, 147.82, 155.38, 160.25; MALDI-TOF calcd for  $C_{69}H_{52}N_4O_2S_2$ : *m/z* 1032.3532; found: *m/z* 1032.3376 [M<sup>+</sup>].

**CT2PYR**: m.p. 247-248 °C, FT-IR (KBr, v, cm<sup>-1</sup>): 3415, 2957, 1711, 1617, 1480, 1355, 1260, 1132, 806; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.23 (6H, t, *J* = 6.9 Hz), 3.41 (4H, q, *J* = 6.6 Hz), 6.57 (1H, s), 6.62 (1H, d, *J* = 8.1 Hz), 7.23-7.35 (4H, m), 7.56 (1H, d, *J* = 6.9 Hz), 7.2-7.82 (4H, m), 7.88 (1H, s), 7.96-8.03 (4H, m), 8.09-8.19 (10H, m), 8.22 (2H, d, *J* = 9.6 Hz), 8.28 (2h, d, *J* = 9.3 Hz), 8.39 (2H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 12.44, 45.21, 110.38, 122.33, 123.88, 124.21, 124.66, 124.75, 125.01, 125.25, 125.52, 125.76, 125.96, 127.28, 127.47, 128.13, 128.83, 128.97, 129.44, 130.43, 131.04, 131.53, 134.14, 136.23, 136.30, 137.00, 138.17, 141.63, 155.47, 160.35; MALDI-TOF calcd for C<sub>65</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: *m*/z 946.2688; found: *m*/z 946.5925 [M<sup>+</sup>].

- 11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- 12. Ning, Z. J.; Zhou, Y. C.; Zhang, Q.; Ma, D. G.; Zhang, J. J.; Tian, H. J. Photochem. Photobiol. A, 2007, 192, 8-16.
- (a) Thangthong, A.; Prachumrak, N.; Namuangruk, S.; Jungsuttiwong, S.; Keawin, T.; Sudyoadsuk, T.; Promarak, V. *Eur. J. Org. Chem.*, **2012**, *27*, 5263-5274. (b) Kamtekar, K. T.; Wang, C.; Bettington, S.; Batsanov, A. S.; Perepichka, I. F.; Bryce, M. R.; Ahn, J. H.; Rabinal, M.; Petty, M. C. J. Mater. Chem., **2006**, *16*, 3823-3835.
- (a) Fink, R.; Heischkel, Y.; Thelakkat, M.; Schmidt, H. -W. Chem. Mater. 1998, 10, 3620-3625. (b) Fenter, P.; Schreiber, F.; Bulović, V.; Forrest, S. R. Chem. Phys. Lett., 1997, 277, 521-526.
- 15. Kartens, T.; Kobs, K. J. Phys. Chem., **1980**, 84, 1871-1872.
- 16. Mitschke, U.; Bäuerle, P. J. Mater. Chem., 2000, 10, 1471-1507.

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