

ARTICLE

Supplementary Information

A twisted double donor in donor-acceptor-donor D₂-D₁-A-D₁-D₂ type emitters yields multicomponent charge-transfer emission

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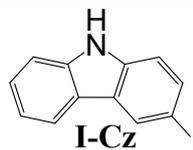
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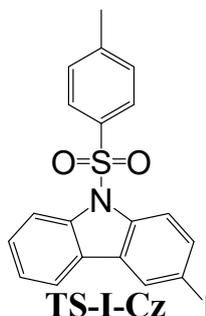
S1. Synthetic procedures

Carbazole (Cz), p-toluenesulfonyl chloride, 4,6-dichloro-2-methylpyrimidine, 4-(diphenylamino)phenylboronic acid KI, KIO₃, KOH, K₂CO₃, Na₂SO₄, Cu, CuI, acetic acid, isopropyl alcohol, acetone, DMF, DMSO and THF were purchased from Aldrich and used as received.



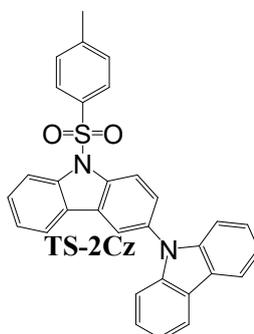
3-Iodocarbazole (I-Cz) was synthesized using the Tucker iodation method, wherein commercially available carbazole (Cz) was reacted with a mixture of KI and KIO₃ in acetic acid [1].

¹H NMR (CDCl₃, 400 MHz, δ, ppm): 8.38 (s, 1H, Ar), 8.05 (s, 1H, NH), 8.00 (d, 1H, J = 8.0 Hz, Ar), 7.65 (d, 1H, J = 8.4 Hz, Ar), 7.46-7.40 (m, 2H, Ar), 7.25-7.20 (m, 2H, Ar).



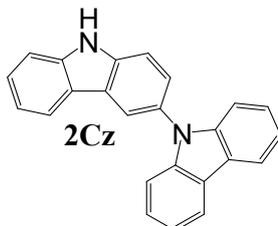
3-Iodo-9-tosylcarbazole (TS-I-Cz) was prepared by reacting 3-iodocarbazole with p-toluenesulfonyl chloride in acetone, following the previously described procedure[2].

¹H NMR (CDCl₃, 400 MHz, δ, ppm): 8.17 (d, 2H, J = 7.8 Hz, Ar), 8.07 (d, 3H, J = 8.2 Hz, Ar), 7.78 (dd, 1H, J = 8.8; 7.6 Hz, Ar), 7.65 (d, 2H, J = 8.4 Hz, Ar), 7.13 (d, 2H, J = 8.0 Hz, Ar), 2.29 (s, 3H, CH₃).



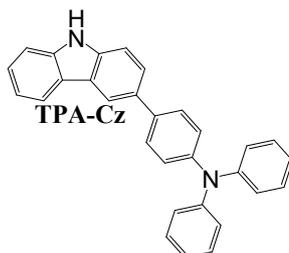
3-(Carbazol-9-yl)-9-tosylcarbazole (TS-2Cz) was synthesized via anUllmann reaction between 3-iodo-9-tosylcarbazole (TS-I-Cz) and carbazole, following a method reported in the literature [3].

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.58 (d, 1H, $J = 8.4$ Hz), 8.42 (d, 1H, $J = 8.8$ Hz), 8.20 (d, 2H, $J = 7.6$ Hz), 8.11 (s, 1H), 7.91 (d, 1H, $J = 8.0$ Hz), 7.85 (d, 2H, $J = 8.0$ Hz), 7.70 (d, 1H, $J = 8.8$ Hz), 7.59 (t, 1H, $J = 8.2$ Hz), 7.46-7.40 (m, 5H), 7.34 (t, 2H, $J = 7.0$ Hz), 7.23 (d, 2H, $J = 8.0$ Hz), 2.36 (s, 3H).



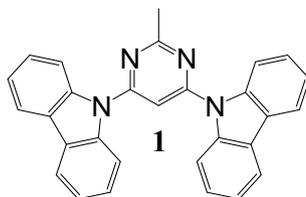
3-(Carbazol-9-yl)-9H-carbazole (**2Cz**) was synthesized by detosylation of 3-(carbazol-9-yl)-9-tosylcarbazole (**TS-2Cz**) using KOH in a mixture of DMSO, THF, and H_2O , following a method reported in the literature [3].

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.24 (d, 3H, $J = 7.2$ Hz), 8.18 (s, 1H), 8.07 (d, 1H, $J = 7.6$ Hz), 7.61-7.56 (m, 2H), 7.52-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.37-7.29 (m, 3H).



3-(4-(Diphenylamino)phenyl)-9H-carbazole (**TPA-Cz**) was synthesized via a Suzuki coupling reaction between 3-iodocarbazole (**I-Cz**) and 4-(diphenylamino)phenylboronic acid, as outlined in the literature [4].

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.18 (s, 1H), 8.02 (d, 1H, $J = 7.6$ Hz), 7.91 (s, 1H), 7.56 (d, 1H, $J = 8.4$ Hz), 7.50 (d, 2H, $J = 8.4$ Hz), 7.34 (d, 3H, $J = 8.0$ Hz), 7.21-7.15 (m, 5H), 7.11-7.06 (m, 6H), 6.94 (t, 2H, $J = 7.2$ Hz).



4,6-Di(carbazol-9-yl)-2-methylpyrimidine (**1**). A mixture of 9H-carbazole (**Cz**) (0.5 g, 2.99 mmol), 4,6-dichloro-2-methylpyrimidine (0.16 g, 0.99 mmol), and dried K_2CO_3 (4.13 g, 29.9 mmol) was stirred in 10 mL of DMSO at 100 °C under a nitrogen atmosphere for 12 hours. Upon completion, monitored by TLC, the reaction mixture was cooled and quenched with ice water. The

product was extracted with chloroform, and the organic extracts were combined and dried over anhydrous Na_2SO_4 . The crude product was purified using silica gel column chromatography with a THF/hexane mixture (1:7, v/v) as the eluent, yielding 0.25 g (59%) of a pale-yellow solid material.

HR-MS (ESI, positive ion mode) m/z $[\text{M}]^+$: calcd for $\text{C}_{29}\text{H}_{21}\text{N}_4$, 425.1769; found, 425.1761.

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.06 (d, 4H, $J = 8.4$ Hz, Ar), 8.01 (d, 4H, $J = 7.6$ Hz), 7.65 (s, 1H, Ar), 7.41 (t, 4H, $J = 7.6$ Hz, Ar), 7.29 (t, 4H, $J = 7.4$ Hz), 2.89 (s, 3H, CH_3)

^{13}C NMR (400 MHz, CDCl_3 , δ , ppm): 169.79, 160.15, 138.85, 126.75, 125.42, 122.31, 120.38, 112.61, 102.73, 26.45.

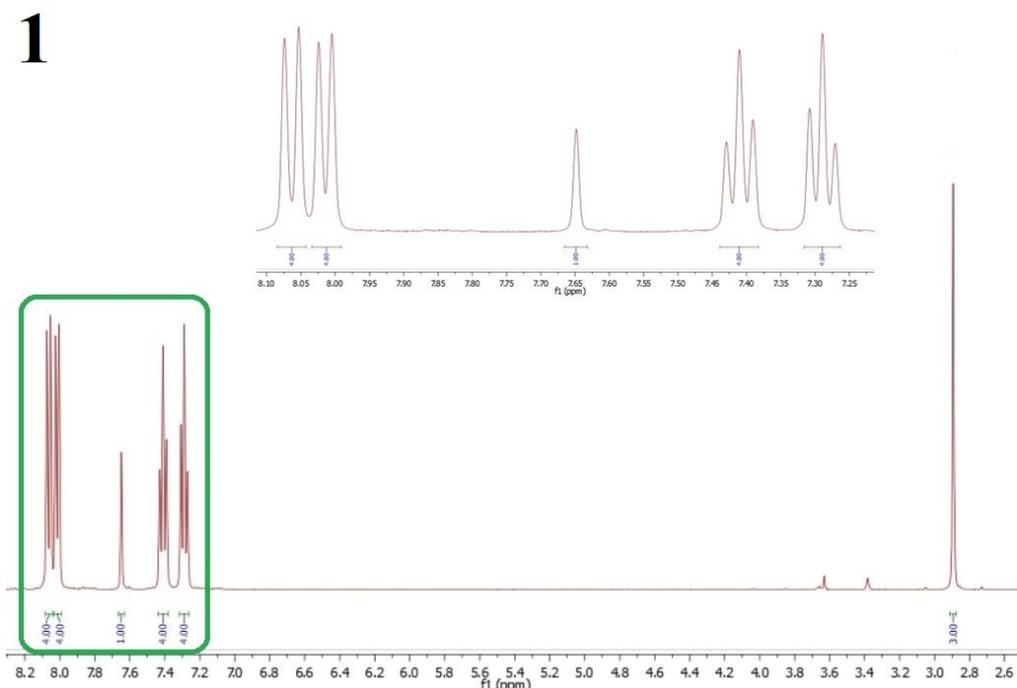
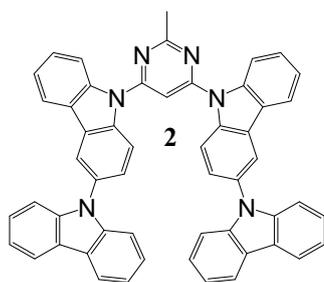


Fig. S1. ^1H NMR spectra of compound **1**.



4,6-Di(3-(carbazol-9-yl)carbazol-9-yl)-2-methylpyrimidine (**2**). A mixture of 3-(carbazol-9-yl)-9H-carbazole (**2Cz**) (0.5 g, 1.51mmol), 4,6-dichloro-2-methylpyrimidine (0.082 g, 0.50mmol), and dried K_2CO_3 (2.08 g, 15.1mmol) was stirred in 10 mL of DMSO at 100 °C under a nitrogen atmosphere for 12 hours. Upon completion, monitored by TLC, the reaction mixture was cooled and quenched with ice water. The product was extracted with chloroform, and the organic extracts were combined and dried over anhydrous Na_2SO_4 . The crude product was purified using silica gel column chromatography with a THF/hexane mixture (1:10, v/v) as the eluent, yielding 0.31 g (83%) of a pale-yellow solid material.

HR-MS (ESI, positive ion mode) m/z $[M]^+$: calcd for $C_{54}H_{35}N_6$, 755.2914; found, 755.2918.

1H NMR (400 MHz, $CDCl_3$, δ , ppm): 8.39 (d, 2H, $J = 7.2$ Hz, Ar), 8.20 (s, 2H, Ar), 8.12-8.08 (m, 6H, Ar), 8.02 (d, 2H, $J = 7.6$ Hz, Ar), 7.84 (s, 1H, Ar), 7.61 (d, 2H, $J = 7.6$ Hz, Ar), 7.50 (t, 2H, $J = 7.8$ Hz, Ar), 7.35-7.32 (m, 10H, Ar), 7.25-7.21 (m, 4H, Ar), 2.99 (s, 3H, CH_3).

^{13}C NMR (400 MHz, $CDCl_3$, δ , ppm): 170.24, 160.16, 141.58, 139.33, 137.94, 132.27, 127.51, 126.65, 126.19, 126.02, 125.04, 123.30, 122.78, 120.88, 120.41, 119.90, 119.31, 114.18, 112.50, 109.75, 102.90, 26.56.

2

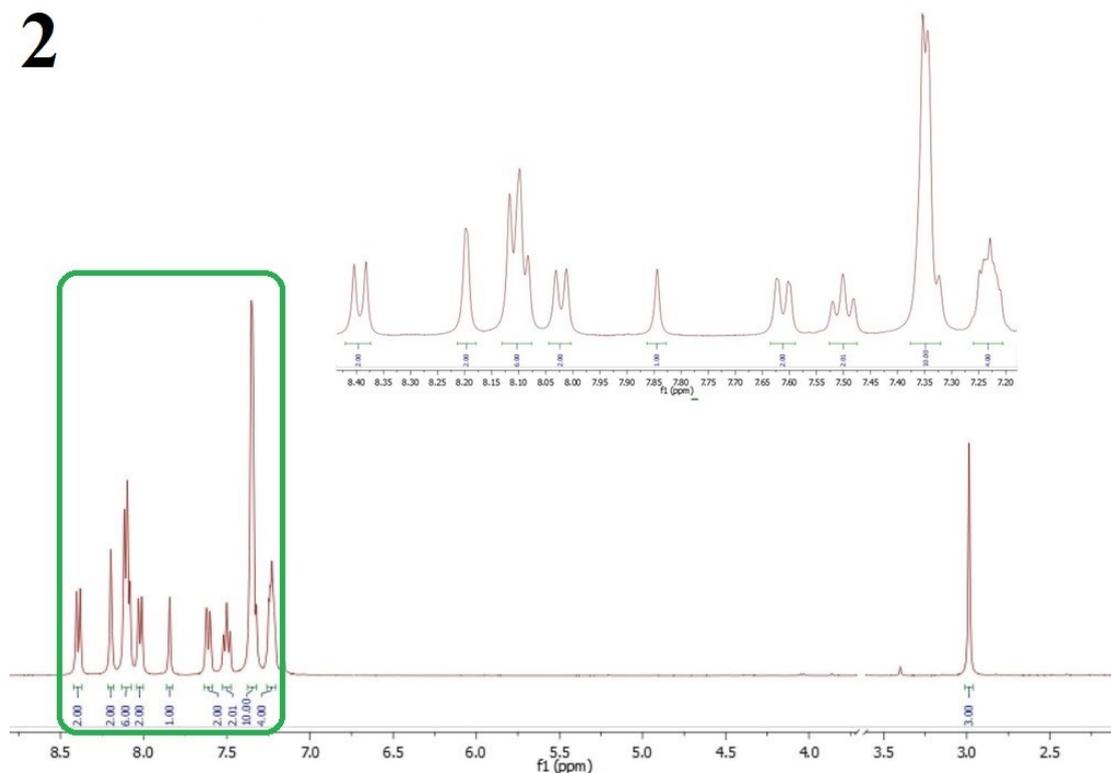
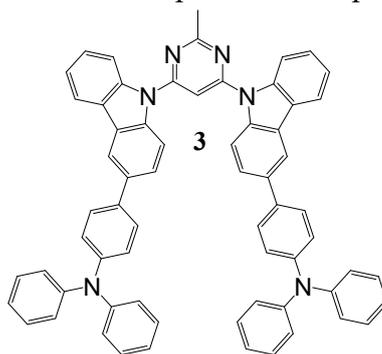
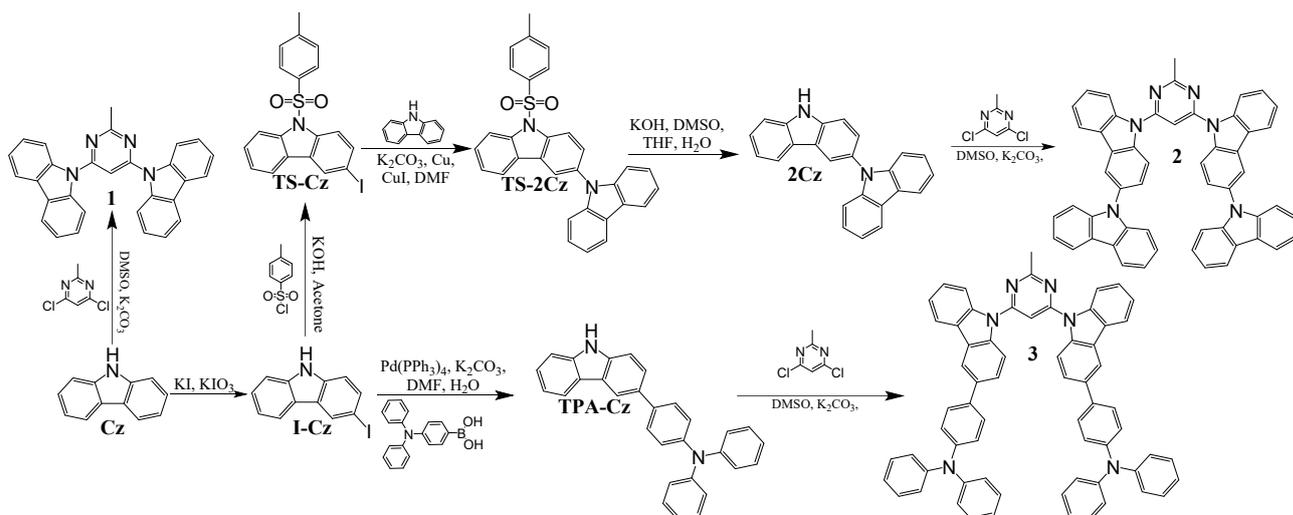


Fig. S2. 1H NMR spectra of compound 2.



4,6-Di(3-(4-(diphenylamino)phenyl)carbazol-9-yl)-2-methylpyrimidine (**3**). A mixture of 3-(4-(diphenylamino)phenyl)-9H-carbazole (**TPA-Cz**) (0.5 g, 1.22mmol), 4,6-dichloro-2-methylpyrimidine (0.066 g, 0.41mmol), and dried K_2CO_3 (1.61 g, 12.2mmol) was stirred in 10 mL of DMSO at 100 °C under a nitrogen atmosphere for 12 hours. Upon completion, monitored by TLC, the reaction mixture was cooled and quenched with ice water. The product was extracted with chloroform, and the organic extracts were combined and dried over anhydrous Na_2SO_4 . The crude



Scheme S1. Synthesis of materials **1-3**.

S2. Spectroscopic measurements

UV-Vis absorption and photoluminescence (PL) spectra of solutions were recorded using an AvaSpec-2048 spectrometer. For PL studies, a thermoelectrical cooling of the CCD detector was applied to reduce noise contribution. Solutions were measured using a 10 mm quartz cuvette; pure solvent was used as a reference. Thin films were measured using quartz or glass substrates; pure substrate was used as a reference. PL emission was excited using solid-state diode lasers operating at 365 and 254 nm. Bandgap was determined at a low-energy cutoff of the absorption spectrum.

Relative PL quantum yield (PLQY) was determined by comparing PL emission of the sample solutions and ethanol solution of anthracene (PLQY=27% [5]) as a reference, using the formulae:

$$PLQY = PLQY_{ref} \frac{PL_{sample}/A(\lambda_{exc})}{PL_{ref}/A_{ref}(\lambda_{exc})} \times \left(\frac{n}{n_{ref}}\right)^2 \quad (1),$$

where PL_{sample} and PL_{ref} are the integral fluorescence of the sample and reference solutions, $A(\lambda_{exc})$ and $A_{ref}(\lambda_{exc})$ are the absorption factors of the sample and reference solutions at excitation wavelength (365 nm), n and n_{ref} are the refractive indices of the sample and reference solutions, respectively. Specifically, solutions with absorption of about or less than 0.1 at excitation wavelength were prepared and measured (Figs. S4 and S5). First, PLQY was determined for toluene solutions of **2** and **3** at $\lambda_{exc}=356$ nm, followed by measurement of PLQY of **1** at $\lambda_{exc}=340$ nm, where PLQY of both anthracene and **3** was taken as a reference. The final PLQY was determined as average of data collected at two different excitation wavelengths.

Ultraviolet photoelectron emission spectra (UPS) were measured using a photoelectron spectrometer at a base pressure of 10^{-10} mbar. Excitation was provided by non-monochromatized He I radiation at $h\nu=21.22$ eV. The HOMO was determined at a low-energy cutoff of the UPS spectrum and the LUMO as HOMO plus bandgap value of the material. The work function WF was

determined from the UPS measurements as the difference between the excitation energy $h\nu$ (21.22 eV) and the spectrum edge of the secondary electrons E_{cutoff} , $WF = h\nu - E_{cutoff}$.

S3. UV-Vis and UPS spectra

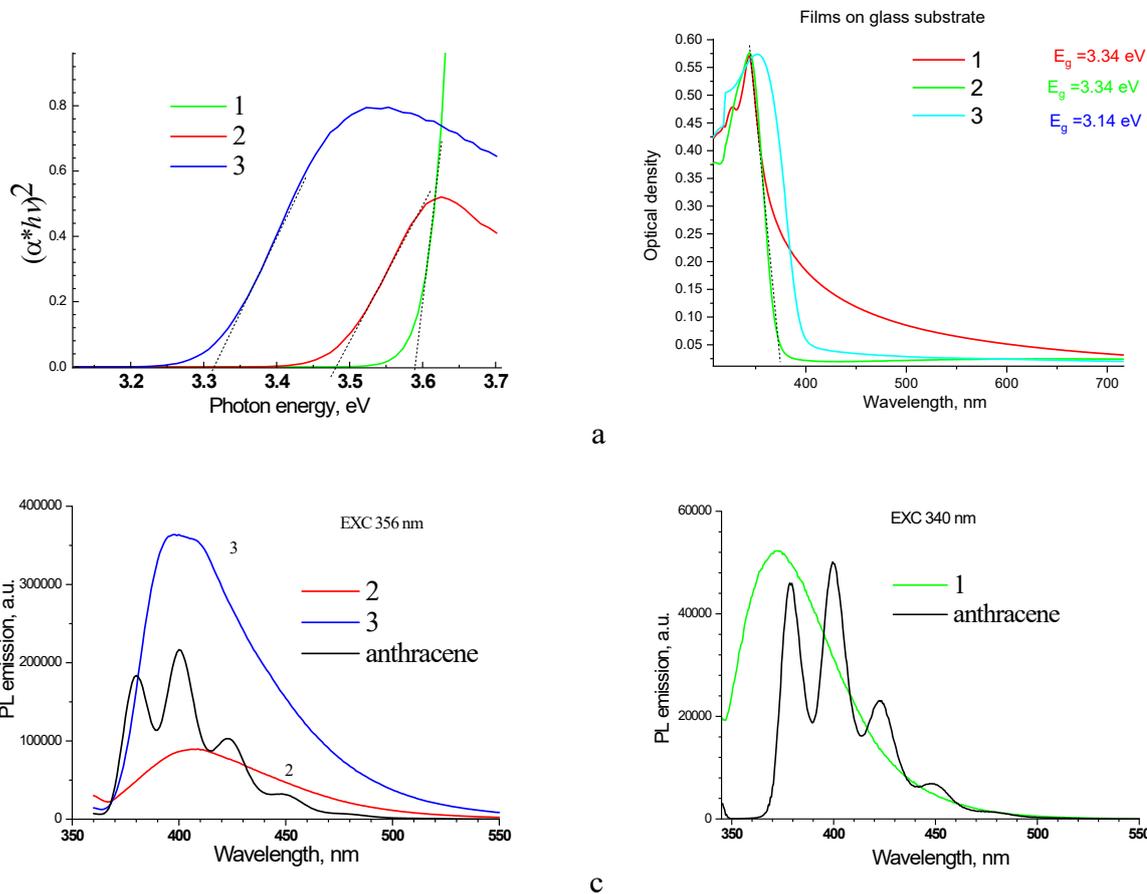
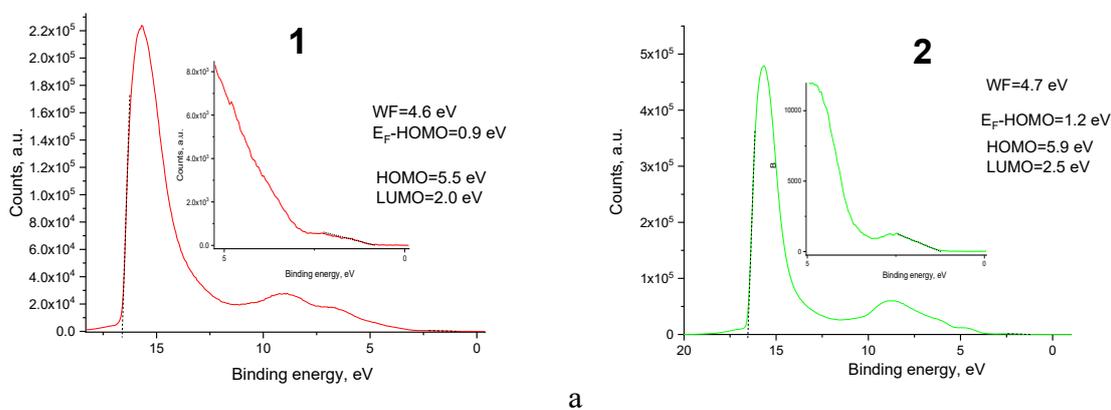
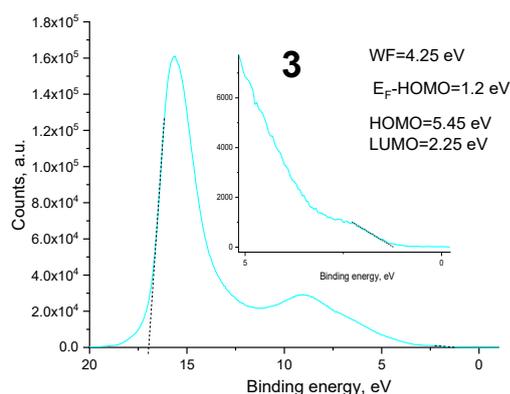


Fig. S4. UV-Vis absorption spectra of (a) toluene solutions (10^{-5} M) and (b) thin films of the materials on glass substrates and (c,d) PL spectra of toluene solutions of 1-3 and ethanol solution of anthracene for measuring PLQY.





c

Fig. S5. UPS spectra of the compounds deposited on ITO substrates. Indicated are HOMO and WF determined from the spectra.

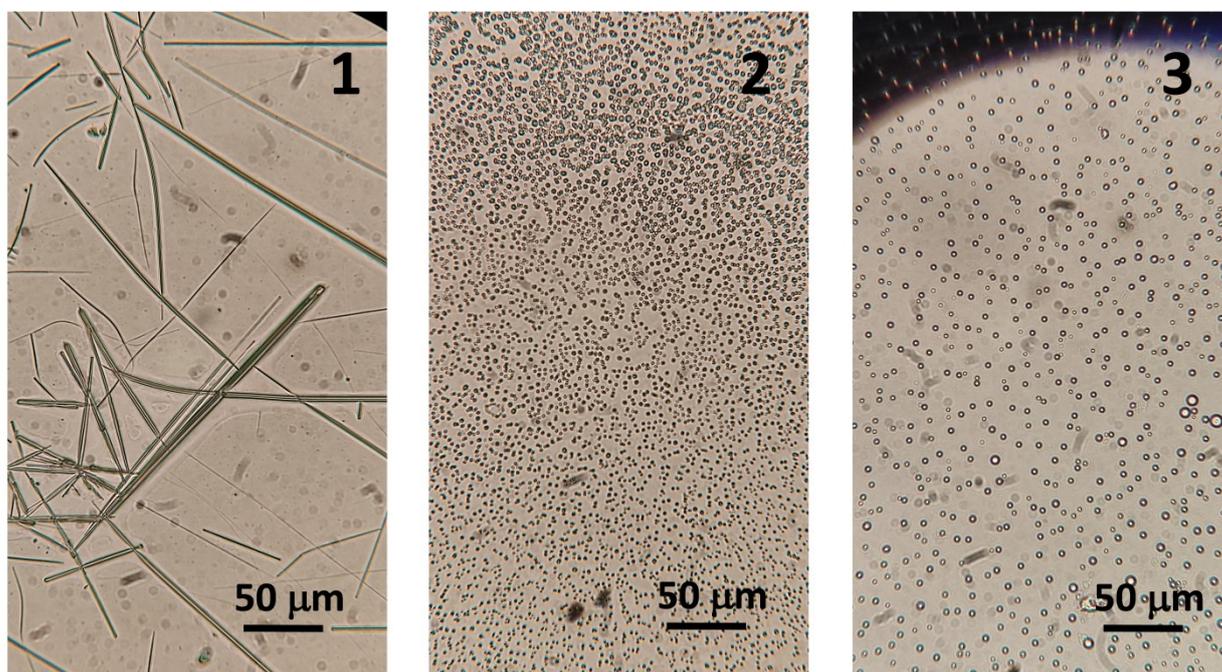


Fig. S6. Optical micrographs of drop-cast neat films of compounds **1-3**. Whiskers seen in **1** indicate that its crystalline phase is favorably formed.

S4. Computational Methodology

All the density functional theory (DFT) and time-dependent (TD)-DFT calculations were performed with the Gaussian 16 software [6]. The optimized ground state (S_0) chemical geometries were found for all conformers. All the vibrational frequencies were verified and no imaginary frequency were found. All of the S_0 -state geometry optimization calculations were carried out using the B3LYP [7] DFT functional with a double- ζ basis set 6-31G(d). The same basis set was employed to perform the fluorescence spectrum simulation. All the DFT and TD-DFT calculations were carried out in the chloroform solvent as used for the experiment. The Polarizable Continuum

Model (PCM) [8] was employed as a commonly used model to consider the solvent effects for excited states of organic compounds. **Table S1** illustrates the fluorescence (λ_{flu}) of all conformers.

Table S1. Fluorescence (λ_{flu}) of the conformers of **1-3**. Oscillator strength, f , is given in parenthesis.

Dye 1				
Conformers #	S1, λ_{flu} in nm, (Oscillator Strength, f)		S ₀ -State Dihedrals	S ₁ -State Dihedrals
1	447.88 (0.0054)		D-A = -19° D-A = 42°	D-A = -19° D-A = 99°
2	463.43 (0.1101)		D-A = -35° D-A = 47°	D-A = -47° D-A = 47°
Dye 2				
1	467.77 (0.1316)	θ_1	D1-A = -38° D1-A = 38°	D1-A = -59° D1-A = 89°
		θ_2	D2-A = 60° D2-A = 0°	D2-A = 67° D2-A = 0°
2	492.16 (0.0010)	θ_1	D1-A = -40° D1-A = 37°	D1-A = -40° D1-A = 64°
		θ_2	D2-A = 58° D2-A = -60°	D2-A = 43° D2-A = -67°
3	539.57 (0.0001)	θ_1	D1-A = 19° D1-A = 39°	D1-A = 19° D1-A = 86°
		θ_2	D2-A = 59° D2-A = -59°	D2-A = 65° D2-A = 137°
Dye 3				
1	517.74 (0.0002)	θ_1	D1-A = 36° D1-A = 5°	D1-A = 92° D1-A = 5°
		θ_2	D2-A = -35° D2-A = 35°	D2-A = -21° D2-A = 34°
2	546.88 (0.0010)	θ_1	D1-A = 33° D1-A = -34°	D1-A = 33° D1-A = -91°
		θ_2	D2-A = -35° D2-A = 35°	D2-A = -35° D2-A = 21°
3	584.04 (0.0007)	θ_1	D1-A = 33° D1-A = -34°	D1-A = -87° D1-A = -63°
		θ_2	D2-A = -15° D2-A = 35°	D2-A = -15° D2-A = 35°

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