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## Article

# Molecular Engineering for the Development of a Discotic Nematic Mesophase and Solid-State Emitter in Deep-Blue OLEDs

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**ADSTRACT:** A unique strategy for the attainment of a discotic nematic (N<sub>D</sub>) mesophase is reported consisting of a central benzene core to which are attached two 4-alkylphenyl and two 4pentylbiphenyl moieties diagonally via alkynyl linkers. The rotational nature and incompatibility of unequal phenylethynyl units led to the disruption of  $\pi - \pi$  interactions within cores that aids to the realization of N<sub>D</sub> phase and favors high solid-state emission. When



used in OLEDs, compounds act as an efficient solid-state pure deep-blue emitter with Commission Internationale de L'Eclairage  $(CIE_{x,y})$  coordinates of (0.16, 0.07).

# INTRODUCTION

Molecular shape is the most important factor that controls the self-organization of the molecules into liquid crystalline (LC) phases. For instance,  $\pi$ -conjugated flat aromatic cores lead to the formation of columnar phases in discotic LCs due to strong core-core interactions.<sup>1</sup> However, the realization of nematic phases formed by discotic molecules (so-called discotic nematic  $(N_D)$  phases) requires flexibility in the molecular structure to disrupt the intercore interactions. In this direction, limited examples are reported in the literature which include triphenylene, naphthalene, truxene, perylene, anthraquinone, and hexa- or penta-alkynylbenzene based systems.<sup>2</sup> Differing from these, herein, we have developed a unique strategy to achieve discotic nematogens by utilizing X-shaped molecules (Figure 1). Such a molecular structure was synthesized previously; however, they failed to show mesomorphism. For example, Ehlers et al. synthesized a molecule with central benzene core connected to four 4-pentylphenyl as rigid arms via alkynyl linkers, which appears as a red-brown liquid.3 Interestingly, the use of four 4-pentylbiphenyl as flexible side linkers to the same core forms a pale yellow solid crystal as reported by Sekine and co-workers.<sup>4</sup> Motivated by these prior reports, we sought to observe any mesomorphism using the combination of 4-alkylphenyl and 4-pentylbiphenyl moieties through alkynyl linkers to the benzene core (Figure 1). Interestingly, using the present strategy, we observed the formation of N<sub>D</sub> mesophases. We believe that the incompatibility of the two unequal side arms to the core is likely responsible for improper packing to the realization of the N<sub>D</sub> mesophase.

Another important feature of such types of multiynes is that they emit in the blue region.<sup>5</sup> Hence, they can also act as blue-



**Figure 1.** Comparison of the present molecular design and state of the material along with its earlier reports.<sup>3,4</sup>

light-emitting materials which are hugely scarce in the area of organic light-emitting diodes (OLEDs). OLEDs have recently gained an immense level of attention due to their widespread application, from small portable devices to flat-panel full-color displays and solid-state lighting sources.<sup>6</sup> To date, pure deepblue OLEDs are very rare in comparison to their red and green complements.<sup>7</sup> In general, most commercial OLEDs rely on vacuum-sublimed devices rather than solution-processed ones.

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Scheme 1. Synthesis of Derivatives of 1<sup>a</sup>



"Reagents and conditions: (i) 3,4-Dihydro-2*H*-pyran (DHP), pyridinium *p*-toluenesulfonate (PPTS), r.t., 12 h. (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, PPh<sub>3</sub>, dry Et<sub>3</sub>N/dry piperidine (2.8:1), 90 °C, 18 h. (iii) *p*-Toluenesulfonic acid (*p*-TsOH), dichloromethane/methanol (2.3:1), r.t., 12 h. (iv) Trifluoromethanesulfonic anhydride (Tf<sub>2</sub>O), piperidine, dichloromethane, r.t., 12 h. (v) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, Et<sub>3</sub>N (dry), 90 °C, 18 h. Yield of 1: 68–70%.

While the performance of vacuum-sublimed OLEDs is unrivalled at present, the process is both costly and materialwasteful.<sup>8</sup> In addition, it is also expensive to fabricate large-area pixels given the size of the evaporator.9 However, the solutionprocessed fabrication of OLEDs such as using ink-jet printing technology could address the underlying limitations of the vacuum-sublimation technique.<sup>10</sup> In this context, using LC molecules consisting of peripheral alkyl chains not only makes them easily solution-processable but also allows for fine-tuning of their central chromophoric part which could serve as a source of pure deep-blue light emission in OLEDs. In this direction, we have synthesized N<sub>D</sub> compounds 1.1 and 1.2 and used them as a solid-state emitter material in solutionprocessable OLEDs. Interestingly, 1.1 showed excellent performance with a maximum external quantum efficiency  $(EQE_{max})$  of 4.0%, and high-quality pure deep-blue emission with  $CIE_{x,y}$  coordinates of (0.16, 0.07), matching closely with the National Television System Committee (NTSC) and High-Definition Television (HDTV) standards.<sup>11</sup>

# RESULTS AND DISCUSSION

The synthetic route of compounds 1.1 and 1.2 is provided in Scheme 1. Detailed synthesis and structural characterization of 1.1–1.2 are outlined in the Experimental Section and the Figures S1–S31. Compound 1.1 was found to produce bright yellow colored crystals when crystallized from hexane solvent at room temperature. The structure of this compound was solved and refined using single-crystal X-ray diffraction data at 100 K in monoclinic unit cell (a = 29.617(2) Å, b = 5.9768(4) Å, c = 33.630(3) Å,  $\beta = 115.121(10)^\circ$ , V = 5390.0(8) Å<sup>3</sup>), C2/c space group with Z = 4 (Z' = 0.5) (CCDC 2047919, Table S1). The inversion center of the molecule (Figures 2a and S32) was found to coincide with the crystallographic center of inversion; hence, half of the molecule was found in the

asymmetric unit. Although a  $-C_5H_{11}$  chain is attached to the aromatic terminals (C15 and C28) of the molecule, these chains have different conformations (Table S2). There are two sets of molecules in the unit cell: One set is marked as red (all the atoms are red), and other set is marked as blue (all the atoms are blue) (Figure 2b). These two sets of molecules are oriented differently in the lattice. The molecules in the red set are parallel to each other and the molecules in the blue set are parallel to each other. The interplanar distance is 7.39 Å in both the set of molecules. The planes are drawn through the central aromatic ring of the red set of molecules and the blue set of molecules (Figure 2c). This figure clearly indicates that the red molecules are parallel to one another and that blue molecules are parallel to one another and the planes through the set of blue molecules and the planes through the set of red molecules intersect at an angle of 64.5°. The same is shown as a scheme in the Figure 2d. This arrangement of molecules further favors to attain the LC state at high temperature (vide infra).

The thermal behavior of **1.1** and **1.2** was characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Both the compounds (**1.1** and **1.2**) exhibited good thermal stability as seen from Figure S33. In DSC (Figure S34a, Table S3), compound **1.1** showed two transitions on heating: One at 179.1 °C ( $\Delta H = 33.0$  kJ/mol) corresponds to the crystal to mesophase, and another at 187.2 °C ( $\Delta H = 1.2$  kJ/mol) relates to mesophase to isotropic transition. On cooling, it also exhibited two transitions. Under POM, **1.1** shows schlieren texture (Figure 3a) upon cooling form isotropic, indicating its nematic LC character of the mesophase.<sup>5a,12</sup> Compound **1.2** exhibited phase transitions similar to those observed for **1.1** (Figures S34b and S35, Table S3).



Figure 2. (a) ORTEP of the molecule with 50% probability ellipsoid; asymmetric unit (gray) is shown with the atom numbering scheme and the symmetry generated part of the molecule 1.1 is shown in yellow (H atoms are excluded for clarity). (b) Packing diagram of the molecule 1.1 viewed down the *b*-axis. (c) Parallel planes drawn through the red molecules and through the blue molecules of 1.1 are shown here in the packing diagram viewed down the *c*-axis. (d) Schematic representation of arrangement of the molecules of 1.1.



Figure 3. (a) POM micrograph of 1.1 at 135.8 °C upon cooling from isotropic liquid (crossed polarizer X 200). (b) XRD pattern of 1.1 at 150 °C (upon cooling) along with the *d*-spacing in the small and wide-angle regime. (c) Schematic representation of the discotic nematic phase of 1.1 where the compound is modeled as the disc.

Furthermore, the quantitative study of compounds **1.1** and **1.2** in the nematic phase is detailed by small- and wide-angle X-ray scattering (SAXS/WAXS) experiments as summarized below. The X-ray diffraction (XRD) pattern of **1.1** (Figure 3b) shows one narrow and one broad peak in the small- and wide-angle regions, respectively. The observed *d*-spacing of the small-angle peak is 24.52 Å which appears due to the average interdisc distance parallel to the disc plane and corresponds to the approximated diameter of the discotic unit. Moreover, the observed *d*-spacing of the wide-angle peak is 5.17 Å which mainly originated from the liquidlike correlation of the molten

chains. Thus, the mesophase of 1.1 is  $N_D$  in nature. The correlation length for the small-angle peak (with a *d*-spacing of 24.52 Å) is 26.38 Å, which corresponds to about one correlated disc unit along disc plane, whereas for the wide-angle peak (with a *d*-spacing of 5.17 Å) the correlation length is 8.64 Å, which reflects about two correlated alkyl chains. This is very much suitable for the nematic phase. The XRD pattern corresponds to the nematic phase of the 1.2 is very similar to that of 1.1 and analyzed in a similar way (Figure S36). The compound 1.1 can be modeled as disc which leads to forming discotic nematic phase (Figure 3c).

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The photophysical characteristics of **1.1** and **1.2** were studied by UV-vis and fluorescence spectroscopy (Figure S37 and S38 and Table S4). Both the compounds exhibited blue emission in solution as well as in the solid state. Furthermore, to study the impact of solvent polarity on the photophysical behavior of **1.1** and **1.2**, we have performed absorption and emission spectroscopy in various solvents. From Figures S39 and S40, we observed that both the compounds (**1.1** and **1.2**) showed very negligible change in absorption spectra, whereas they showed a weak positive solvatochromism effect in the emission spectra (Table S5). This can be attributed to the symmetrical molecular structures of **1.1** and **1.2**, which are also evidenced from the single-crystal X-ray diffraction data analysis (*vide supra*).

Compound 1.1 and 1.2 exhibited HOMO/LUMO at -5.51/-3.45 eV and -5.48/-3.44 eV, respectively, as determined from their electrochemical characteristics, measured by cyclic voltammetry (Figure S41 and Table S6). Furthermore, to visualize the electronic distribution of frontier molecular orbitals of 1.1 and 1.2, density functional theory (DFT) calculation was performed. It revealed that both HOMO and LUMO are spatially distributed at the alternate positions of the molecules (1.1 and 1.2), having contributions from the central as well as peripheral aromatic rings (Figure S42).

Encouraged by the excellent thermostability and photophysical properties of compounds 1.1 and 1.2, the electroluminescence (EL) properties were assessed in multilayer solution-processed OLEDs with the configuration of ITO/ PEDOT:PSS (40 nm)/CBP: x wt % 1.1 or 1.2 (x = 0.5, 1.0, 3.0, and 5.0) (20 nm)/TPBi (35 nm)/LiF (1 nm)/Al (150 nm). The energy level alignment diagram of the studied devices is displayed in Figure 4a, and the performances are



**Figure 4.** (a) Schematic energy-level diagram. (b) Normalized EL spectra (inset shows blue emission and CIE plot). (c) Current density–voltage–luminance (J-V-L) and (d) current efficiency–luminance–power efficiency (CE–L–PE) performance plots of **1.1**-and **1.2**-based OLED devices (doped with CBP host at 1.0 wt %).

summarized in Tables 1 and S7. The presence of long side chains in compounds 1.1 and 1.2 renders their better solubility in organic solvents and allows the OLED devices to be solution-processable along with the good miscibility within the CBP host matrix to form a homogeneous emissive layer. The topography image of CBP:1.1 and CBP:1.2 films (at 1.0 wt %)

Table 1. Electroluminescence Properties of Solution-						
Processed OLED Devices Based on Emitters 1.1 and 1.	2					
Doped with CBP Host at 1.0 wt %						

emitter	$\operatorname{turn-on}_{\operatorname{voltage}}(\mathrm{V})^{a}$	$\frac{\text{PE}_{\text{max}}/\text{CE}_{\text{max}}/\text{EQE}_{\text{max}}}{(\text{Im W}^{-1}/\text{cd A}^{-1}/\%)^{6}}$	CIE coordinates <sup>c</sup>	$L_{ m max} \over ( m cd/m^2)$
1.1	3.2	1.5/2.1/4.0	(0.16, 0.07)	1098
1.2	3.1	1.4/1.6/2.9	(0.16, 0.07)	1202
Waltaga	(1	$a = 1$ and $m^{-2}$ b Marin		affer all and and

<sup>a</sup>Voltage (luminance >1 cd m<sup>-2</sup>). <sup>b</sup>Maximum power efficiency ( $PE_{max}$ ), current efficiency ( $CE_{max}$ ), luminance ( $L_{max}$ ), and external quantum efficiency ( $EQE_{max}$ ). <sup>c</sup>CIE coordinates at 100 cd m<sup>-2</sup>.

was measured by atomic force microscopy (AFM) in tapping mode. From AFM, the root means square (RMS) roughness of CBP:1.1 and CBP:1.2 film was recorded as 0.6 and 0.9 nm, respectively, indicating good miscibility (homogeneity phase) between emitters and the CBP host.<sup>13</sup> The representative AFM image of CBP:1.1 film is shown in Figure S43.

The normalized EL spectra, current density-voltageluminance (J-V-L), current efficiency-luminance-power efficiency (CE-L-PE) characteristics of the **1.1** and **1.2** based OLED devices are shown in Figure 4b-d, and performances are summarized in Tables 1 and S7 and Figures S44 and S45. Figure 4b displays the EL spectra of the **1.1**- and **1.2**-based OLEDs. The deep-blue emissive devices display the EL peak at 420 nm which is consistent with their optical band gap energies and manifest closely with the PL spectra of the film.

Noticeably, both devices present low turn-on voltage (luminance >  $1 \text{ cd/m}^2$ ) in the range of 3.1-3.2 V which can be rationalized by well-matched energy levels of the compounds with the host and leads to favorable charge injection, migration, and recombination. The presented CIE results of the devices are much close to the CIE coordinates of (0.14, 0.08) enjoined by the NTSC and HDTV standards.<sup>11</sup>

The 1.1-based device demonstrated excellent performance with a maximum external quantum efficiency  $(EQE_{max})$  of 4.0%, a maximum luminance  $(L_{max})$  of 1098 cd/m<sup>2</sup>, and particularly high-quality pure deep-blue emission with CIE coordinates of (0.16, 0.07). The EQE can still remain at 3.1%, even at a brightness of 100  $cd/m^2$  (Figure S46). In contrast, the 1.2 device shows an EQE<sub>max</sub> of 2.9%, a  $L_{max}$  of 1202 cd/m<sup>2</sup>, and a maximum current efficiency (CE $_{\rm max})$  of 1.6 cd/A. The photoluminescence quantum yield (PLQY,  $\Phi_{\text{PL}})$  of 1.1 and 1.2 in doped films were 85.11 and 79.31%, respectively, recorded using an integrating sphere under a N<sub>2</sub> atmosphere, consistent with the aforementioned results. In particular, it is also noteworthy that the triplet energy  $(E_{\rm T})$  of the compounds is smaller than that of CBP host, which favorably enables effective host-guest energy/exciton transfer and hence a better device performance. The recorded  $E_{\rm T}$  of compounds 1.1 and 1.2 are 2.38 and 2.28 eV, respectively. The better OLED performance of 1.1 is consistent with the small energy transfer barrier (0.17 eV) with CBP (2.55 eV) that ensures efficient harvesting of excitons with favorable charge balance and energy transfer in the devices.<sup>14</sup>

To have further insight into the energy transfer process, transient photoluminescence (PL) decay characteristics were studied, as shown in Figure S47. The fluorescence lifetimes of the CBP:1.1 (1.0 wt %) and CBP:1.2 (1.0 wt %) systems exhibit a single exponential decay with a lifetime of 2.22 and 2.18 ns, respectively. Understanding the potential for efficient exciton generation, we measured the theoretical exciton

utilization efficiency (EUE), which was calculated by employing the equation; EQE =  $\gamma \cdot \eta_{out} \cdot \Phi_{PL} \cdot EUE$ ,<sup>15</sup> where  $\gamma$  is the charge balance factor (in the case of perfect charge balance,  $\gamma =$ 1) and  $\eta_{out}$  is the out-coupling efficiency (0.2–0.3). A high EUE of 23.5% is achieved in the case of **1.1**, indicating a high degree of exciton participation in the radiative transition process. On the other hand, **1.2** exhibited a comparatively low EUE of 19.5%, which is in agreement with the OLED performance.

## CONCLUSION

In conclusion, we have developed a unique strategy for the synthesis of a discotic nematic liquid crystal. The discotic molecules exhibited blue emission in solution as well as in the solid state. Upon application in solution-processable OLEDs as an emitter, compound **1.1** showed pure deep-blue emission with a maximum EQE of 4.0% and CIE coordinate of (0.16, 0.07) which is very close to NTSC and HDTV standards. The present study opens a platform to the development of new discotic nematic materials for their utility in optoelectronic devices.

## EXPERIMENTAL SECTION

**Measurements and Characterization.** The instrumental details for structural characterization (NMR, HRMS, and FT-IR), thermal characterization (polarized optical microscopy (POM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD)), photophysical studies (UV–vis and fluorescence), electrochemical (cyclic voltammetry), and electroluminescence (OLEDs) characterization are similar to those mentioned in our previous papers.<sup>13</sup>

**Synthesis Details.** *Compound* **5.** In a 10 mL single-necked round-bottomed flask (RBF), 2,5-dibromobenzene-1,4-diol (2 g, 7.46 mmol) and 3,4-dihydro-2H-pyran (2.68 mL, 29.37 mmol) were mixed and stirred for 12 h in the presence of pyridinium *p*-toluenesulfonate (13.40 mg, 0.05 mmol). After that, the reaction mixture was extracted with dichloromethane (DCM) from a mixture of DCM/water. Then, the extracted organic layer was dried over anhydrous sodium sulfate. After concentrating, it was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the product as a beige amorphous solid in 92% yield (2.98 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 (s, 2H), 5.37 (b, 2H), 3.89 (t, *J* = 10.84 Hz, 2H), 3.64–3.61 (m, 2H), 2.07–1.82 (m, 6H), 1.75–1.60 (m, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.7, 121.3, 112.2, 97.6, 61.9, 30.2, 25.2, 18.3. HRMS (ESI) *m/z*: (M + Na)<sup>+</sup> calcd for C<sub>16</sub>H<sub>20</sub>Br<sub>2</sub>NaO<sub>4</sub> 458.9606. Found 458.9595.

Compound 4.1. In a 100 mL two-necked RBF, compound 5 (1.70 g, 3.89 mmol) was dissolved in dry Et<sub>3</sub>N/piperidine (40/15 mL) under N<sub>2</sub> atmosphere. To this solution were added  $Pd(PPh_3)_4$  (73.95 mg, 0.064 mmol), CuI (27.48 mg, 0.144 mmol), and PPh3 (36.73 mg, 0.140 mmol) at room temperature. Then 1-ethynyl-4-pentylbenzene (1.72 g, 10 mmol) was added dropwise under a N<sub>2</sub> atmosphere. The mixture was refluxed at 90 °C (oil bath) for 18 h with stirring under nitrogen atmosphere. The reaction mixture was then cooled, quenched with 5 M aqueous HCl, diluted with distilled water, and extracted with DCM. The combined DCM extracts were washed with water and dried over anhydrous sodium sulfate. The reaction mixture was dried in rotary evaporator and then was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the product as a dark-yellow semisolid in 75% yield (1.82 g). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ :  $\delta$  7.43 (d, J = 7.92 Hz, 4H), 7.25 (s, 2H), 7.16 (d, J = 8.00 Hz, 4H), 5.51 (b, 2H), 4.07-4.01 (m, 2H), 3.66-3.63 (m, 2H), 2.61 (t, J = 7.72 Hz, 4H), 2.15–2.08 (m, 2H), 2.03–1.99 (m, 2H), 1.93– 1.86 (m, 2H), 1.74-1.68 (m, 4H), 1.65-1.60 (m, 6H), 1.36-1.30 (m, 8H), 0.89 (t, J = 6.66 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz,  $CDCl_3$ ):  $\delta$  152.1(8), 152.1(1), 143.5, 131.5, 128.6, 120.7, 120.5, 120.4, 115.5, 115.4, 97.4, 97.2, 95.0, 85.4(4), 85.4(3), 61.7, 36.0, 31.5,

31.0, 30.4, 25.4, 22.6, 18.4(6), 18.4(4), 14.1. HRMS (ESI) m/z: (M + H)<sup>+</sup> calcd for C<sub>42</sub>H<sub>51</sub>O<sub>4</sub> 619.3787. Found 619.3793.

*Compound* **4.2**. Compound **4.2** was synthesized by following same procedure as used in synthesizing **4.1**. It was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the product as yellow solid in 73% yield (1.84 g) from 1.7 g of **5**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (d, *J* = 7.96 Hz, 4H), 7.25 (s, 2H), 7.16 (d, *J* = 8.00 Hz, 4H), 5.51 (b, 2H), 4.07–4.01 (m, 2H), 3.66–3.63 (m, 2H), 2.61 (t, *J* = 7.70 Hz, 4H), 2.17–2.09 (m, 2H), 2.05–1.97 (m, 2H), 1.93–1.85 (m, 2H), 1.77–1.68 (m, 4H), 1.64–1.59 (m, 6H), 1.35–1.28 (m, 12H), 0.88 (t, *J* = 6.56 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.1(8), 152.1(2), 143.5, 131.5, 128.6, 120.7, 120.5, 120.4, 115.5, 115.4, 97.4, 97.2, 95.0, 85.4(5), 85.4(3), 61.8, 36.0, 31.8, 31.3, 30.4, 29.0, 25.4, 22.7, 18.4(7), 18.4(5), 14.2. HRMS (ESI) *m/z*: (M + H)<sup>+</sup> calcd for C<sub>44</sub>H<sub>55</sub>O<sub>4</sub> 647.4100. Found 647.4083.

*Compound* **3.1**. In the presence of *p*-toluenesulfonic acid (281.53 mg, 1.48 mmol), compound **4.1** (915.88 mg, 1.84 mmol) was stirred in DCM/methanol (50:22 mL) for 18 h. Then the reaction mixture was diluted with distilled water and extracted with DCM. The extracted organic layer was dried over anhydrous sodium sulfate. The extracted organic layer was concentrated in rotary evaporator and then was purified by column chromatography (silica gel, hexane/ethyl acetate) to get the product as yellow-brown solid in 90% yield (600 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (d, *J* = 7.76 Hz, 4H), 7.19 (d, *J* = 7.80 Hz, 4H), 7.01 (s, 2H), 5.50 (s, 2H), 2.63 (t, *J* = 7.70 Hz, 4H), 1.66–1.60 (m, 4H), 1.37–1.30 (m, 8H), 0.89 (t, *J* = 6.56 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.0, 144.5, 131.7, 128.8, 119.2, 116.6, 111.6, 98.1, 82.4, 36.0, 31.5, 31.0, 22.6, 14.1. HRMS (ESI) *m*/*z*: (M + H)<sup>+</sup> calcd for C<sub>32</sub>H<sub>35</sub>O<sub>2</sub> 451.2637. Found 451.2640.

*Compound* **3.2**. Compound **3.2** was synthesized by following same procedure as that used in synthesizing **3.1**. It was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the product as yellow-brown solid in 86% yield (636.36 mg) from 1 g of **4.2**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (d, *J* = 8.16 Hz, 4H), 7.19 (d, *J* = 8.16 Hz, 4H), 7.01 (s, 2H), 5.49 (s, 2H), 2.63 (t, *J* = 7.70 Hz, 4H), 1.65–1.60 (m, 4H), 1.35–1.31 (m, 12H), 0.89 (t, *J* = 6.78 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.0, 144.5, 131.7, 128.8, 119.2, 116.7, 111.6, 98.1, 82.4, 36.1, 31.8, 31.3, 29.0, 22.7, 14.2. HRMS (ESI) *m*/*z*: (M + H)<sup>+</sup> calcd for C<sub>34</sub>H<sub>39</sub>O<sub>2</sub> 479.2950. Found 479.2935.

Compound 2.1. Compound 3.1 (400 mg, 0.89 mmol) was added to dry DCM (40 mL) and degassed for 15 min. Pyridine (0.32 mL, 3.99 mmol) was then added, and the solution was cooled to 0 °C. To the cooled solution was added dropwise trifluoromethanesulfonic anhydride (0.50 mL, 2.66 mmol), and the mixture was warmed to room temperature and kept for 24 h. The mixture was quenched with 10% aqueous HCl. The reaction mixture was then diluted with distilled water and extracted with DCM. The combined DCM extracts were washed with water and dried over anhydrous sodium sulfate. After concentrating, the product was purified by column chromatography (neutral alumina, hexane/ethyl acetate) to give the product as bright yellow solid in 82% yield (520.24 mg). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.52–7.50 (m, 6H), 7.21 (t, J = 7.92 Hz, 4H), 2.63 (t, J = 7.72 Hz, 4H), 1.66-1.59 (m, 4H), 1.37-1.28 (m, 8H), 0.90 (t, J = 6.62 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>): δ 148.1, 145.4, 132.0, 128.8, 126.1, 120.3, 119.9, 118.5, 117.1, 100.7, 80.9, 36.1, 31.5, 31.0, 22.6, 14.1. <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>): δ -73.30. IR (Neat film, KBr):  $\nu_{\rm max}/{\rm cm}^{-1}$  2958.6, 2924.3, 2873.3, 2857.0, 2222.3, 1521.0, 1489.0, 1428.7, 1401.4, 1244.6, 1215.6, 1209.3, 1139.0, 1122.7, 907.5, 850.0, 794.3, 733.5, 666.3, 604.7, 514.6, 465.2. HRMS (ESI) m/z: (M + H)<sup>+</sup> calcd for  $C_{34}H_{33}F_6O_6S_2$  715.1623. Found: 715.1613.

*Compound* **2.2**. Compound **2.2** was synthesized by following same procedure that as used in synthesizing **2.1**. It was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the product as bright yellow solid in 86% yield (467.08 mg) from 350 mg of **3.2**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52–7.50 (m, 6H), 7.21 (t, *J* = 8.12 Hz, 4H), 2.63 (t, *J* = 7.70 Hz, 4H), 1.65–1.55 (m, 4H), 1.37–1.25 (m, 12H), 0.89 (t, *J* = 6.64 Hz, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.1, 145.5, 132.0, 128.8, 126.1, 120.3, 119.8, 118.5,

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117.1, 100.7, 80.9, 36.1, 31.8, 31.2, 29.0, 22.7, 14.2. <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>):  $\delta$  -73.29. IR (Neat film, KBr):  $\nu_{max}/cm^{-1}$  2959.6, 2927.4, 2873.0, 2856.2, 2223.0, 1521.4, 1489.4, 1427.7, 1402.3, 1244.4, 1214.7, 1208.0, 1139.7, 1123.4, 910.0, 850.8, 826.1, 729.4, 666.5, 604.2, 514.5, 465.6. HRMS (ESI) *m*/*z*: (M + H)<sup>+</sup> calcd for C<sub>36</sub>H<sub>37</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub> 743.1936. Found 743.1923.

Compound 1.1. In a 100 mL two-necked RBF was added dry triethylamine (50 mL), and the flask was purged with N<sub>2</sub> gas for 20 min. Then, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (147.40 mg, 0.21 mmol), CuI (20 mg, 0.105 mmol), PPh<sub>3</sub> (27.61 mg, 0.105 mmol), compound 2.1 (350 mg, 0.49 mmol), and 4-ethynyl-4'-pentyl-1,1'-biphenyl<sup>16</sup> (486.78 mg, 1.96 mmol) were added sequentially in the solvent-filled RBF, and the flask was purged with N<sub>2</sub> gas for 20 min. The reaction mixture was refluxed at 90 °C (oil bath) for 36 h. After cooling the reaction mixture to room temperature, the solvent was removed by rotary evaporation. Then, organic layer was extracted by performing the dichloromethane (DCM)/water extraction. The DCM extracts were dried over anhydrous sodium sulfate. After concentrating, the target material (1.1) was purified by using column chromatography (neutral alumina, hexane) to get the product as yellow solid in 70% yield (312.38 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (s, 2H), 7.62 (dd, J = 24.33 Hz, 8.31 Hz, 8H), 7.53 (dd, J = 19.56 Hz, 8.04 Hz, 8H), 7.27 (d, J = 8.04 Hz, 4H), 7.18 (d, J = 8.04 Hz, 4H), 2.67-2.62 (m, 8H), 1.69-1.61 (m, 12H), 1.37–1.34 (m, 12H), 0.92–0.89 (m, 12H). <sup>13</sup>C{1H} NMR (126 MHz, CDCl<sub>3</sub>): δ 144.1, 142.8, 141.5, 137.7, 134.9, 132.3, 131.8, 129.1, 128.7, 127.0(3), 127.0(1), 125.5, 125.4, 121.7, 120.3, 95.9, 95.5, 88.4, 87.2, 38.3, 36.1, 35.7, 31.6(9), 31.6(2), 31.3(9), 31.3(0), 31.0, 29.8, 22.7, 22.6, 14.1(9), 14.1(7). IR (Neat film, KBr):  $\nu_{\rm max}$ / cm<sup>-1</sup> 3028.3, 2954.8, 2928.3, 2870.1, 2856.3, 2205.7, 1688.9, 1604.1, 1515.7, 1499.8, 1465.7, 1407.8, 1378.3, 1276.1, 1261.4, 1187.6, 1109.2, 1018.4, 1004.8, 970.7, 895.8, 826.5, 810.6, 764.4, 749.7. HRMS (MALDI) m/z: (M + H)<sup>+</sup> calcd for C<sub>70</sub>H<sub>71</sub> 911.5556. Found 911.5526.

Compound 1.2. Compound 1.2 was synthesized by following same procedure as that used in synthesizing 1.1. It was purified by column chromatography (neutral alumina, hexane) to give the product as yellow solid in 68% yield (300 mg) from 350 mg of 2.2. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (s, 2H), 7.62 (dd, J = 24.63 Hz, 8.25 Hz, 8H), 7.53 (dd, J = 19.8 Hz, 8.04 Hz, 8H), 7.27 (d, J = 8.04 Hz, 4H), 7.18 (d, J = 7.98 Hz, 4H), 2.67–2.62 (m, 8H), 1.67–1.60 (m, 8H), 1.38-1.30 (m, 20H), 0.92-0.87 (m, 18H). <sup>13</sup>C{1H} NMR (126 MHz, CDCl<sub>3</sub>): δ 144.1, 142.8, 141.5, 137.7, 134.9, 132.3, 131.8, 129.1, 128.7, 127.0(3), 127.0(1), 125.5, 125.3 121.7, 120.0, 95.9, 95.5, 88.4, 87.2, 36.1, 35.7, 31.8, 31.6, 31.3(5), 31.3(1), 29.1, 22.7(5), 22.7(1), 14.2, 14.1. IR (Neat film, KBr):  $\nu_{\rm max}/{\rm cm}^{-1}$  3207.7, 2954.7, 2927.0, 2869.6, 2856.0, 2205.1, 1687.8, 1603.7, 1514.4, 1498.0, 1465.3, 1407.3, 1377.5, 1268.4, 1256.9, 1189.8, 1115.2, 1004.2, 969.3, 896.1, 826.24, 808.4, 764.6, 750.4. HRMS (MALDI) m/z: (M + H)<sup>+</sup> calcd for C72H75 939.5869. Found 939.5837.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00742.

Detailed characterizations of all the new compounds (PDF)

# **Accession Codes**

CCDC 2047919 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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