Novel, yellow-emitting anthracene/fluorene oligomers: synthesis and characterization

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Abstract—A novel series of highly soluble and strongly yellow fluorescent with well-controlled, alternative anthracene, and fluorene units were successfully synthesized by a Pd/Cu-catalyzed Sonogashira coupling reaction and characterized. Their thermal stabilities, electrochemical behaviors, and photophysical properties were investigated. These oligomers might be used as models to study structure–property relationship for their corresponding polymers and applied in optoelectronics devices as materials themselves.
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1. Introduction

Conjugated oligomers have triggered intense investigations from both academic and industrial laboratories[1] due to their promising applications, such as light-emitting diodes (OLEDs),[2] solar cells,[3] field-effect transistors (FETs),[4] and models[5] to understand the structure–property relationships of their analogous polydisperse polymers. In contrast to polymers, monodisperse conjugated oligomers are characterized by a well-defined and uniform molecular structure as well as superior chemical purity, which would offer improved stability and sharper emission bands.[6] Development of synthetic methodology makes it possible to design a variety of soluble monodisperse oligomers, which permit color and charge injection tunable through the conjugation length control, as well as the introduction of functional groups to the parent π-conjugated system.[7] For example, palladium-catalyzed cross-coupling reaction of terminal alkynes with arylhalides (the Sonogashira reaction) provides an efficient and versatile tool to extend π–π conjugation in organic compounds, affording simplified molecular structures compared with their alkene analogues due to the lack of *Z/E* isomerism of the double bonds.[8] And many ethynylene-linked oligomers of special properties have been designed and synthesized.[9] To these ethynylene-extended arenes and heteroarenes, it has been proved to be of the function as nanoscale 'molecular wires', with the extent of intramolecular conjugation dependent upon the topology of the π-system and the molecular length.[10]

Both fluorene and anthracene are well-known blue fluorophores and their derivatives have been widely used as emitting materials or else. Though random poly(fluorene-*co*-anthracene)s have been reported,[11] to the best of our knowledge, few oligomers or polymers based on well-controlled alternative fluorene and anthracene structures are reported. Therefore, in this paper, we would like to report the synthesis and characterization of a series of monodisperse, ethynylene-linked oligomers with well-defined, alternative fluorene and anthracene structures. These oligomers could be used as models to study structure–property relationship for their corresponding polymers or be applied in optoelectronic devices as materials themselves.

2. Results and discussion

A Pd/Cu-catalyzed Sonogashira coupling reaction was used as a key reaction to build ethylnylene-linked molecules. Synthetic approach of necessary intermediates are outlined in Scheme 1. Our strategy to the target molecules started from 9-iodo-anthracene (**1**) and 9,10-diiodo-anthracene (**4**). Pd/Cu-catalyzed coupling of **1** and 3-methyl-1-butyn-3-ol provided **2**, which was followed by a base-promoted deprotection to afford 9-ethynyl-anthracene (**3**) in 85% total yield. Similar procedures were performed from **4** to obtain 9,10-diethynyl-anthracene (**6**) in 64% total yield. Treatment of **3** with 3 equiv of 2,7-diiodo-9,9-diheptyl-9*H*-fluorene (**7**)[12] in the presence of CuI, Pd(PPh$_3$)$_2$Cl$_2$, Ph$_3$P, and NEt$_3$ afforded intermediate **8** in 84% yield after separation by column chromatography. Compound **8** was then converted to **10** in 78% total yield after cross-coupling and deprotection procedure. Compound **10** reacted with 3 equiv of **4** in the presence of Pd/Cu catalyst to afford **11** in 66% yield. Analogous

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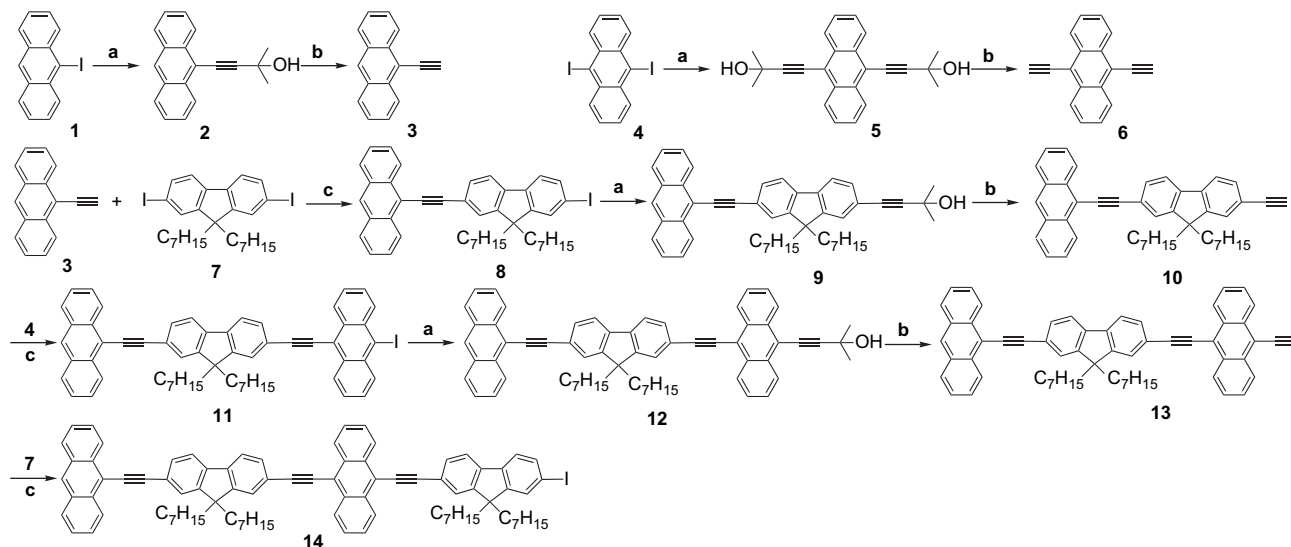
Scheme 1. (a) 3-Methyl-1-butyn-3-ol, CuI, Pd(PPh₃)₂Cl₂, Ph₃P, NEt₃, N₂, reflux; (b) KOH, 2-propanol, reflux; and (c) CuI, Pd(PPh₃)₂Cl₂, Ph₃P, NEt₃, N₂, reflux.

procedures were performed step by step to get intermediate **14** from **11** in 28% total yield.

In order to facilitate the synthesis of longer oligomers, we tried to gain compound **18**, which could serve as a core of oligomers with longer molecular length after a bicoupling with monoiodide (Scheme 2). Coupling of 9,10-diiodo-anthracene (**4**) with an equal amount of 3-methyl-1-butyn-3-ol yielded compound **15** in 72% yield, which was followed by a further coupling with **16**[13] giving compound **17** in 65% yield. Compound **18** was produced by the final base-promoted deprotection of **17**, which was indicated by thin layer chromatography. However, it was hard to be isolated because it was unstable when exposed to air in solid states. It was destroyed quickly when we run column chromatography. In fact, we found that compounds **6** and **13** were also unstable, especially for compound **6**.

The final couplings of anthracene/fluorene oligomers are illustrated in Scheme 3. **DAF** and **TATF** were obtained in 89, and 78% yields by treating **16** with 2 equiv of **1** and **11**, respectively, in the presence of CuI, Pd(PPh₃)₂Cl₂, Ph₃P, and NEt₃. **TADF** and **PATF** were obtained in 55 and 38% yields by treating newly prepared **6** with 2 equiv of **8** and **14**, respectively, under the same conditions. Moreover, an additional oligomer **TATFC** was synthesized (48% yield) by coupling intermediate **14** with 3,6-diethynyl-9-p-tolyl-9H-carbazole (**19**)[14] under the same conditions. The existence of 3,6-substituted carbazole core introduced a V shape to the molecule. All the final oligomers were characterized by NMR and element analysis. However, their mass spectra could not be detected by MALDI-TOF mass spectroscopy. All of the oligomers as well as intermediates were solid. Due to the presence of the flexible n-heptyl substituents,

all of these synthesized compounds exhibited excellent solubility in common organic solvents, such as CH₂Cl₂, CHCl₃, THF, and toluene. This is helpful for easier preparation and purification in the synthetic procedure leading to the sufficiently long rod length as well as easier fabrication in the procedures of optoelectronic device preparation.

Thermal properties of these oligomers were examined through differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) in N₂ at a heating rate of 10 °C/min, and these results are listed in Table 1. The decomposition temperatures (T_ds) of these oligomers were in the range of 386–426 °C, with 5% loss of initial weight, while their melting points were not detected. And the glass transition temperatures (T_gs) of oligomer **DAF**, **TADF**, **TATF**, and **PATF** were 101, 115, 119, and 122 °C, respectively, which gradually increased as the main chain length increased.

Electrochemical properties of oligomers were analyzed by cyclic voltammetry (CV) in the CH₂Cl₂ in the presence of 0.1 M Bu₄NPF₆ as supporting electrolyte. The results are listed in Table 1. Oligomers exhibited irreversible oxidation peaks that shift positively from 1.22 to 1.69 V with the increment of the oligomer length. On the basis of the onset potential for the oxidation and the band gap determined from the optical absorption threshold, the HOMO and LUMO energy levels of oligomers were calculated in the range of −5.43 to −5.61 eV and −2.76 to −3.29 eV (Table 1), respectively, with a steady increment as the anthracene unit accumulated.

The photophysical properties of oligomers were examined by UV–vis and photoluminescence (PL) spectroscopy in dilute CH₂Cl₂ solutions and the results are listed in Table 1.
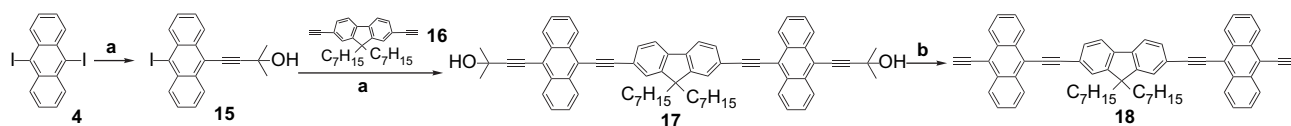
Scheme 2. (a) 3-Methyl-1-butyn-3-ol, CuI, Pd(PPh₃)₂Cl₂, Ph₃P, NEt₃, N₂, reflux and (b) KOH, 2-propanol, reflux.
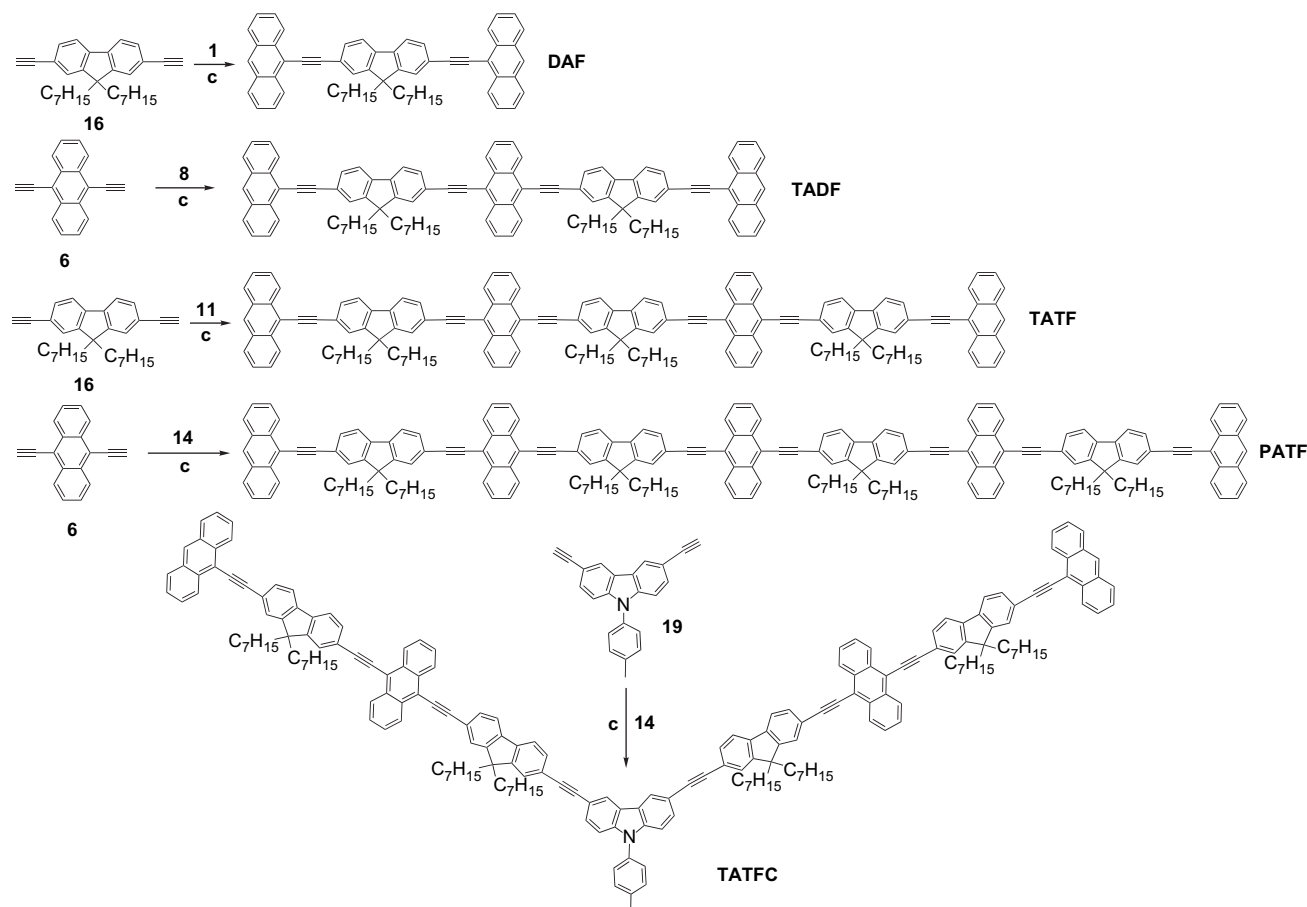
Scheme 3. (c) CuI, Pd(PPh$_3$)$_2$Cl$_2$, Ph$_3$P, NEt$_3$, N$_2$, reflux.

The UV–vis absorption and PL spectra of oligomers in solutions are presented in Figure 1. **DAF** exhibited a maximum absorption peak at 446 nm, while those oligomers with 9,10-diethynyl-anthracene-linked sub-structure (**TADF**, **TATF**, **PATF**, and **TATFC**) exhibited strongly red-shifted maximum absorption peaks in the range of 501–512 nm. Similar phenomena were also observed for those emission spectra. **DAF** emitted blue light with a main peak at 460 nm, while **TADF**, **TATF**, and **PATF** emitted bright yellow light with main peaks at 518, 524, and 528 nm, respectively, with a wavelength slightly red-shifted as the molecular size increased. However, **TATFC** exhibited a main emission peak at 517 nm, which was almost identical to that of **TADF**. This should be due to their similar efficient conjugation length[12,15] of both oligomers. Large red shifts in both absorption and emission could be attributed to the introduction of 9,10-diethynyl-anthracene. Moreover, relative short Stokes' shifts (14–17 nm) for these oligomers in CH$_2$Cl$_2$ solutions were observed, which indicated little loss of energy. The fluorescence quantum yields of these oligomers were measured in degassed cyclohexane using the standard 9,10-diphenylanthrecene (Φ=0.95 in cyclohexane)[16] for **DAF** and 9,10-bis(phenylethynyl)anthracene (Φ=1.0 in cyclohexane)[17] for the other oligomers. **DAF** exhibited comparable higher quantum yield (0.72) than those of the other three oligomers (0.56–0.68). Quantum yields

Table 1. Optical, thermal, and electrochemical properties of compounds

	Abs.[a] (nm)		Em. (nm)		Φ[b]	Stokes' shift	fwhm[c]	E_g[d]	E_{onset}^{ox} [e]	HOMO/LUMO[f]	T_g/T_d[g]
	CH$_2$Cl$_2$	Film	CH$_2$Cl$_2$	Film		(nm)	(nm)	(eV)	(V)	(eV)	(°C)
DAF	446	447	460 (486)	474	0.72	14	18	2.67	1.03	−5.43/−2.76	101/386
TADF	501	502	518 (550)	(525) 555	0.61	17	25	2.35	1.08	−5.48/−3.13	115/410
TATF	507	509	524 (557)	(539) 560	0.59	17	24	2.33	1.12	−5.52/−3.19	119/421
PATF	512	513	528 (560)	(543) 570	0.56	16	22	2.31	1.21	−5.61/−3.29	122/426
TATFC	502	506	517 (550)	(530) 564	0.68	15	24	2.35	1.05	−5.45/−3.10	126/424

[a] Maximum absorption wavelength in dilute CH$_2$Cl$_2$ solutions (∼10^{-6} M).
[b] Measured in cyclohexane solutions.
[c] Full width at half emission maximum in dilute CH$_2$Cl$_2$ solutions (∼10^{-6} M).
[d] Determined from UV–vis absorption spectra.
[e] E_{onset}^{ox}=onset oxidation potential; potentials versus Ag/AgCl, working electrode Pt, 0.1 M Bu$_4$NPF$_6$–CH$_2$Cl$_2$, scan rate 100 mV/s.
[f] HOMO=E_{onset}^{ox}+4.4 eV; LUMO=HOMO−E_g eV.
[g] Measured by DSC analysis and TGA analysis in N$_2$ at a heating rate of 10 °C/min.
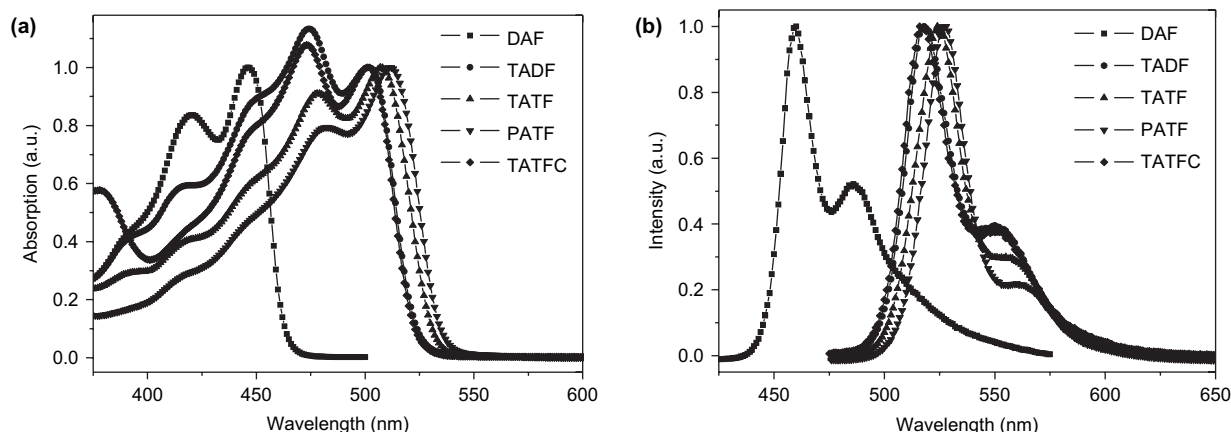
Figure 1. UV–vis absorption (a) and PL (b) spectra of oligomers in CH$_2$Cl$_2$ solutions.

of these oligomers became lower with the insertion of 9,10-diethynyl-anthracene moieties.

In thin neat films, absorption spectra were almost identical to those in CH$_2$Cl$_2$ solutions but with a slight bathochromical shift (1–2 nm), which indicated that these compounds exhibited very similar conformations in both solution and solid states. In the case of emission spectra in neat films, **DAF** exhibited an emission band at 474 nm. **TADF**, **TATF**, **PATF**,

and **TATFC** exhibited main emission bands in the range of 555–570 nm. Figure 2 displays the absorption and PL spectra of **TATF** in thin neat films as an example. The emissions in solid states were red-shifted with respect to those in solutions, which was ascribed to the enhanced molecular interaction in solid states. The morphological property of **TATF** film was investigated by atomic force microscopy (AFM). The one-layer film of **TATF** spin-coated on SiO$_2$/Si was measured. The large square image (2.00×2.00 μm) showed that the film was uniform (left in Fig. 3). And the height between the highest and the deepest parts of the film was roughly 2 nm (right in Fig. 3).
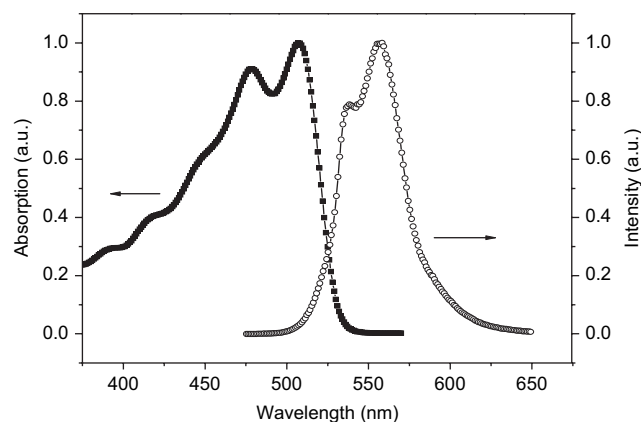
Figure 2. Absorption and PL spectra of **TATF** in neat film.

3. Conclusions

In summary, we had successfully synthesized and fully characterized a series of novel oligomers with well-controlled, alternative anthracene, and fluorene structure. Yellow emission as well as high quantum yields could be approached by incorporating 9,10-diethynyl-anthracene into the molecular backbone. These synthesized compounds might be used as models to study structure–property relationship for their corresponding polymers or applied in optoelectronic devices directly. Further study will be focused on their applications in devices.
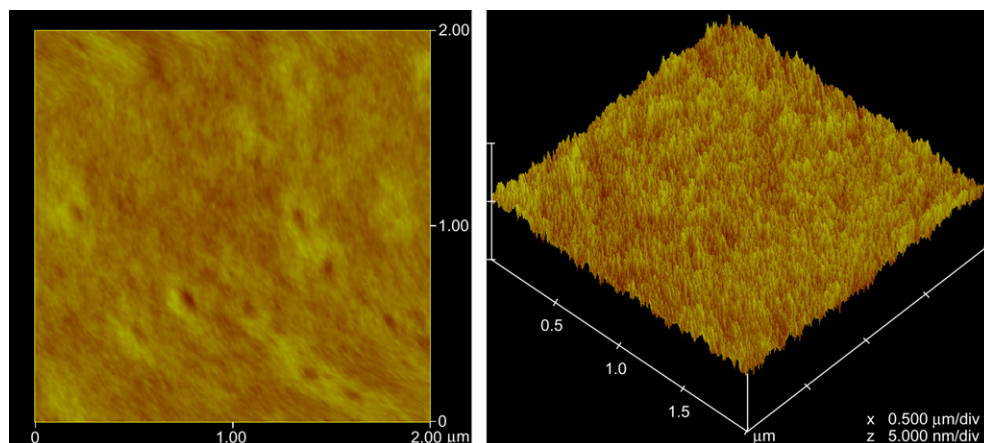
Figure 3. Atomic force microscopy (AFM) image of **TATF** film spin-coated on SiO$_2$/Si.

4. Experimental

4.1. General information

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating in the FT mode. Five percent w/v solutions in chloroform-*d* were used to obtain NMR spectra. TMS was used as an internal standard. IonSpec HiResMALDI was used to obtain mass spectra. Fluorescence measurements were made with a RF-5301pc spectrofluorometer (Shimadzu, Kyoto, Japan) equipped with a xenon lamp. UV–vis absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. NETZSCH STA 409 PG/PC was used to measure the thermal performances of the compounds. Cyclic voltammetric measurements were performed with CHI660A electrochemical workstation, using Pt working electrode, an auxiliary Pt electrode, and an Ag/AgCl reference electrode. The solvents were distilled before use. Commercially available reagents were used without further purification unless otherwise.

4.1.1. General procedure for the synthesis of the compounds (8, 11, 14, DAF, TADF, TATF, PATF, and TATFC).

These compounds were obtained following an essentially similar procedure. The mass spectra of **DAF**, **TADF**, **TATF**, **PATF**, and **TATFC** could not be detected using IonSpec HiResMALDI. An illustrative example was provided for **8**.

4.1.1.1. Compound 8. Compounds **3** (2 g, 0.01 mol), **7** (19 g, 0.03 mol), cuprous iodide (0.1 g, 5 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.035 g, 0.05 mmol), triphenylphosphine (0.05 g, 0.2 mmol), dry triethylamine (300 mL) were placed in a 500-mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography. In this way, 5.5 g (80% yield) of **8** was obtained. ^{1}H NMR δ CDCl$_3$: 0.66 (br, 4H), 0.80 (t, 6H, J=7.0 Hz), 1.08 (br, 12H), 1.17–1.19 (m, 4H), 1.97–2.04 (m, 4H), 7.47 (d, 1H, J= 8.0 Hz), 7.53 (t, 2H, J=7.5 Hz), 7.63 (t, 2H, J=7.5 Hz), 7.68–7.77 (m, 5H), 8.03 (d, 2H, J=8.5 Hz), 8.44 (s, 1H), 8.71 (d, 2H, J=7.5 Hz) ppm; ^{13}C NMR δ CDCl$_3$: 14.31, 22.82, 23.96, 29.18, 30.15, 32.02, 40.49, 55.77, 86.98, 93.44, 101.98, 117.61, 120.18, 121.97, 122.77, 125.97, 126.87, 127.06, 127.95, 129.00, 131.21, 131.49, 132.38, 132.86, 136.28, 140.34, 140.83, 150.68, 153.69 ppm; MS (MALDI) (*m/z*): 688.8 (M$^+$).

4.1.1.2. Compound 11. Yield 67%. ^{1}H NMR δ CDCl$_3$: 0.78–0.84 (m, 10H), 1.15–1.23 (m, 16H), 2.15–2.18 (m, 4H), 7.56–7.59 (m, 2H), 7.67–7.21 (m, 6H), 7.78 (s, 2H), 7.85 (br, 4H), 8.08 (d, 2H, J=8.5 Hz), 8.49 (s, 1H), 8.57–8.59 (m, 1H), 8.62–8.64 (m, 1H), 8.71–8.73 (m, 4H) ppm; ^{13}C NMR δ CDCl$_3$: 14.29, 22.83, 24.08, 29.25, 30.25, 32.05, 40.68, 55.80, 86.75, 87.14, 102.12, 103.27, 103.68, 117.67, 120.50, 122.33, 122.35, 122.83, 126.00, 126.10, 126.14, 126.90, 127.11, 127.62, 127.75, 127.83, 127.98, 128.25, 128.57, 129.03, 130.63, 131.29, 131.55, 132.92, 133.08, 133.29, 133.87, 134.35, 141.12, 141.50, 151.68, 151.73 ppm; MS (MALDI) (*m/z*): 889.1 (M$^+$).

4.1.1.3. Compound 14. Yield 52%. ^{1}H NMR δ CDCl$_3$: 0.67 (br, 4H), 0.75–0.82 (m, 16H), 1.10–1.20 (m, 32H), 1.98–2.04 (m, 4H), 2.12–2.16 (m, 4H), 7.49 (d, 1H, J= 8.0 Hz), 7.55 (t, 2H, J=7.0 Hz), 7.65 (t, 2H, J=7.5 Hz), 7.71–7.78 (m, 11H), 7.82 (d, 4H, J=4.0 Hz), 8.05 (d, 2H, J=8.0 Hz), 8.46 (s, 1H), 8.74 (d, 2H, J=9.0 Hz), 8.78–8.81 (m, 4H) ppm; ^{13}C NMR δ CDCl$_3$: 14.31, 22.84, 23.98, 24.09, 29.18, 29.22, 29.26, 30.17, 30.26, 32.03, 32.06, 40.50, 40.70, 55.80, 55.81, 87.14, 87.32, 87.37, 93.56, 104.00, 117.68, 118.78, 118.87, 120.25, 120.50, 122.03, 122.44, 122.58, 122.80, 126.00, 126.04, 126.13, 126.89, 127.13, 127.62, 127.64. 127.98, 129.02, 131.29, 131.33, 131.54, 132.44, 132.91, 136.33, 140.31, 141.15, 141.47, 151.69, 151.72, 153.73 ppm; MS (MALDI) (*m/z*): 1272.8 (M$^+$).

4.1.1.4. Compound DAF. Yield 89%. ^{1}H NMR δ CDCl$_3$: 0.75–0.80 (m, 10H), 1.12–1.20 (m, 16H), 2.12–2.15 (m, 4H), 7.54 (t, 4H, J=7.5 Hz), 7.65 (t, 4H, J=7.5 Hz), 7.74 (s, 2H), 7.81 (br, 4H), 8.05 (d, 4H, J=8.5 Hz), 8.46 (s, 2H), 8.74 (d, 4H, J=9.0 Hz) ppm; ^{13}C NMR δ CDCl$_3$: 14.30, 22.84, 24.07, 29.25, 30.26, 32.06, 40.70, 55.78, 87.06, 102.16, 120.44, 122.69, 126.00, 126.13, 126.89, 127.12, 127.95, 129.02, 131.26, 131.55, 132.91, 141.23, 151.66 ppm. IR (KBr): 2189.6 cm^{-1} (C≡C stretch). Anal. calcd for C$_{59}$H$_{54}$: C, 92.87; H, 7.13. Found: C, 92.88; H, 7.10.

4.1.1.5. Compound TADF. Yield 55%. ^{1}H NMR δ CDCl$_3$: 0.76–0.81 (m, 20H), 1.12–1.21 (m, 32H), 2.13–2.16 (m, 8H), 7.55 (t, 4H, J=7.5 Hz), 7.65 (t, 4H, J= 7.5 Hz), 7.72–7.74 (m, 4H), 7.76 (d, 4H, J=5.0 Hz), 7.83 (d, 8H, J=5.0 Hz), 8.05 (d, 4H, J=9.5 Hz), 8.46 (s, 2H), 8.74 (d, 4H, J=9.0 Hz), 8.80–8.82 (m, 4H) ppm; ^{13}C NMR δ CDCl$_3$: 14.31, 22.85, 24.09, 29.26, 30.27, 32.07, 40.71, 55.79, 87.13, 87.40, 102.14, 104.00, 117.67, 118.85, 120.50, 122.46, 122.80, 126.01, 126.13, 126.15, 126.90, 127.11, 127.15, 127.16, 127.98, 129.03, 131.69, 131.34, 131.54, 132.45, 132.91, 141.15, 141.47, 151.70, 151.72 ppm. IR (KBr): 2185.4 cm^{-1} (C≡C stretch). Anal. calcd for C$_{98}$H$_{86}$: C, 93.14; H, 6.86. Found: C, 93.10; H, 6.88.

4.1.1.6. Compound TATF. Yield 78%. ^{1}H NMR δ CDCl$_3$: 0.77–0.82 (m, 30H), 1.13–1.21 (m, 48H), 2.13–2.17 (m, 12H), 7.54–7.57 (m, 4H), 7.64–7.67 (m, 4H), 7.72–7.77 (m, 14H), 7.82–7.85 (m, 12H), 8.05 (d, 4H, J=9.0 Hz), 8.47 (s, 2H), 8.74–8.75 (m, 4H), 8.81–8.83 (m, 8H) ppm; ^{13}C NMR δ CDCl$_3$: 14.31, 22.86, 24.10, 29.26, 30.28, 32.08, 40.72, 55.82, 55.84, 87.16, 87.40, 87.48, 102.15, 103.98, 104.02, 117.70, 118.85, 118.90, 120.51, 120.57, 122.47, 122.60, 122.82, 126.01, 126.15, 126.18, 126.91, 127.16, 127.67, 127.99, 129.03, 131.31, 131.35, 131.38, 131.56, 132.48, 132.93, 141.17, 141.42, 141.50, 151.71, 151.74, 151.77 ppm. IR (KBr): 2185.4 cm^{-1} (C≡C stretch). Anal. calcd for C$_{149}$H$_{142}$: C, 92.59; H, 7.41. Found: C, 92.60; H, 7.37.

4.1.1.7. Compound PATF. Yield 38%. ^{1}H NMR δ CDCl$_3$: 0.76–0.82 (m, 40H), 1.14–1.20 (m, 64H), 2.15–2.17 (m, 16H), 7.54–7.57 (m, 4H), 7.65–7.68 (m, 4H), 7.73–7.77 (m, 22H), 7.83–7.85 (m, 14H), 8.06 (d, 4H, J=8.0 Hz), 8.47 (s, 2H), 8.75 (d, 4H, J=8.5 Hz), 8.81–8.83 (m, 12H) ppm; ^{13}C NMR δ CDCl$_3$: 14.29, 14.34, 22.86, 24.13, 29.26, 30.28, 32.08, 40.71, 55.84, 55.87, 87.18, 87.42, 87.45, 87.49, 102.17, 103.99, 104.01, 104.04, 117.74,

118.14, 118.87, 118.90, 118.93, 120.51, 120.58, 122.52, 122.63, 122.86, 126.02, 126.21, 126.91, 127.16, 127.69, 129.04, 131.31, 131.37, 131.39, 131.60, 132.51, 132.96, 141.19, 141.44, 141.52, 151.74, 151.77, 151.80 ppm. IR (KBr): 2185.4 cm^{-1} (C≡C stretch). Anal. calcd for $C_{194}H_{186}$: C, 92.55; H, 7.45. Found: C, 92.56; H, 7.41.

4.1.1.8. Compound TATFC. Yield 48%. ^{1}H NMR δ CDCl$_3$: 0.74 (br, 16 H), 0.78–0.83 (m, 24H), 1.12–1.22 (m, 64H), 2.09–2.16 (m, 16H), 2.52 (s, 3H), 7.38 (d, 2H, $J=8.5$ Hz), 7.44–7.48 (m, 4H), 7.53–7.56 (m, 4H), 7.62–7.67 (m, 10H), 7.72–7.76 (m, 16H), 7.81–7.83 (m, 12H), 8.05 (d, 4H, $J=8.5$ Hz), 8.41 (s, 2H), 8.47 (s, 2H), 8.74 (d, 4H, $J=9.0$ Hz), 8.80–8.82 (m, 8H) ppm; ^{13}C NMR δ CDCl$_3$: 14.30, 21.53, 22.84, 24.08, 29.25, 29.27, 30.26, 30.30, 32.06, 32.09, 40.70, 40.73, 55.68, 55.80, 87.12, 87.7, 87.40, 89.40, 91.26, 102.14, 103.96, 104.06, 110.47, 115.23, 117.69, 118.80, 118.90, 120.37, 120.50, 122.26, 122.47, 122.78, 122.90, 123.22, 124.32, 125.99, 126.12, 126.13, 126.14, 126.20, 126.89, 127.12, 127.19, 127.96, 129.02, 130.26, 130.94, 130.98, 131.29, 131.33, 131.54, 132.44, 132.91, 134.44, 140.60, 141.16, 141.41, 141.46, 141.60, 151.48, 151.66, 151.69, 151.72 ppm. IR (KBr): 2185.4 cm^{-1} (C≡C stretch). Anal. calcd for $C_{199}H_{191}N$: C, 92.05; H, 7.41; N, 0.54. Found: C, 92.07; H, 7.37; N, 0.51.

4.1.2. General procedure for the synthesis of compounds (9 and 12). Both compounds were obtained following an essentially similar procedure. An illustrative example was provided for **9**.

4.1.2.1. Compound 9. Compounds **8** (678 mg, 1 mmol), 3-methyl-1-butyn-3-ol (126 mg, 1.5 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis(triphenylphosphine)-palladium(II) (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), dry triethylamine (100 mL) were placed in a 150-mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 8 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/ methylene chloride as eluent) to get **9** (82% yield). ^{1}H NMR δ CDCl$_3$: 0.65 (br 4H), 0.80 (t, 6H, $J=7.5$ Hz), 1.08 (br, 12H), 1.16–1.20 (m, 4H), 1.68 (s, 6H), 2.00–2.06 (m, 5H), 7.42–7.45 (m, 2H), 7.53 (t, 2H, $J=7.5$ Hz), 7.62–7.69 (m, 4H), 7.73–7.78 (m, 2H), 8.04 (d, 2H, $J=8.0$ Hz), 8.45 (s, 1H), 8.72 (d, 2H, $J=8.5$ Hz) ppm; ^{13}C NMR δ CDCl$_3$: 14.29, 22.83, 23.97, 29.22, 30.23, 31.84, 32.05, 40.62, 55.60, 66.04, 83.32, 86.96, 94.21, 102.10, 117.68, 120.15, 120.34, 121.71, 122.59, 125.98, 126.05, 126.35, 126.86, 127.09, 127.93, 128.99, 131.08, 131.18, 131.52, 132.88, 140.96, 141.14, 151.32, 151.52 ppm; MS (MALDI) (m/z): 644.2 (M$^+$).

4.1.2.2. Compound 12. Yield 63%. ^{1}H NMR δ CDCl$_3$: 0.74–0.80 (m, 10H), 1.12–1.19 (m, 16H), 1.86 (s, 6H), 2.11–2.15 (m, 4H), 2.32 (br, 1H), 7.54 (t, 2H, $J=7.5$ Hz), 7.62–7.69 (m, 6H), 7.74 (s, 2H), 7.81 (br, 4H), 8.04 (d, 2H, $J=8.0$ Hz), 8.45 (s, 1H), 8.55 (d, 2H, $J=9.0$ Hz), 8.75 (t, 4H, $J=9.5$ Hz) ppm; ^{13}C NMR δ CDCl$_3$: 14.30, 22.83, 24.06, 29.24, 30.24, 32.00, 32.05, 40.68, 55.78, 79.31, 87.13, 87.16, 102.11, 103.79, 107.09, 118.96, 120.49,

122.39, 122.79, 125.98, 126.11, 126.89, 127.03, 127.08, 127.13, 127.27, 127.33, 127.55, 127.63, 127.97, 128.45, 129.04, 131.28, 131.32, 131.51, 132.26, 132.41, 132.90, 141.12, 141.47, 151.67, 151.68 ppm; MS (MALDI) (m/z): 844.1 (M$^+$).

4.1.3. General procedure for the synthesis of the compounds (10 and 13). Both compounds were obtained following an essentially similar procedure. An illustrative example is provided for **10**.

4.1.3.1. Compound 10. Compounds **9** (500 mg), KOH (500 mg), and 2-propanol (100 mL) were placed in a 150-mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 4 h. The solvent was then removed and the crude product was purified by column chromatography (silica gel, hexane/methylene chloride as eluent) to afford **10** (75% yield). ^{1}H NMR δ CDCl$_3$: 0.65–0.66 (m, 4H), 0.76 (t, 6H, $J=7.5$ Hz), 1.08 (br 12H), 1.16–1.20 (m, 4H), 2.01–2.04 (m, 4H), 3.17 (s, 1H), 7.50–7.54 (m, 4H), 7.63 (t, 2H, $J=7.5$ Hz), 7.68 (d, 1H, $J=7.5$ Hz), 7.70 (s, 1H), 7.73–7.78 (m, 2H), 8.02 (d, 2H, $J=7.5$ Hz), 8.43 (s, 1H), 8.72 (d, 2H, $J=7.5$ Hz) ppm; ^{13}C NMR δ CDCl$_3$: 14.29, 22.81, 23.99, 29.21, 30.21, 32.04, 40.57, 55.60, 77.59, 84.87, 87.04, 102.04, 120.21, 120.44, 120.99, 122.76, 125.97, 126.07, 126.83, 126.86, 127.07, 127.96, 129.00, 131.21, 131.51, 131.54, 132.88, 140.99, 141.46, 151.34, 151.62 ppm; MS (MALDI) (m/z): 586.0 (M$^+$).

4.1.3.2. Compound 13. Yield 51%. ^{1}H NMR δ CDCl$_3$: 0.76–0.81 (m, 10H), 1.13–1.21 (m, 16H), 2.13–2.16 (m, 4H), 4.10 (s, 1H), 7.55 (t, 2H, $J=7.5$ Hz), 7.65–7.71 (m, 6H), 7.76 (s, 2H), 7.82 (br, 4H), 8.05 (d, 2H, $J=8.0$ Hz), 8.40 (s, 1H), 8.65 (d, 2H, $J=9.0$ Hz), 8.74–8.79 (m, 4H) ppm; ^{13}C NMR δ CDCl$_3$: 14.30, 22.84, 24.07, 29.25, 30.25, 32.05, 40.69, 55.78, 80.71, 87.07, 87.14, 90.12, 102.11, 103.99, 117.31, 117.65, 119.56, 120.49, 122.32, 122.81, 125.92, 125.99, 126.11, 126.14, 126.89, 127.07, 127.09, 127.34, 127.35, 127.56, 127.97, 129.01, 131.28, 131.35, 131.52, 132.18, 132.89, 132.97, 141.11, 141.52, 151.67, 151.69 ppm; MS (MALDI) (m/z): 786.8 (M$^+$).

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