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Preparation and photoluminescence of *p*-terphenyl derivatives containing cyano groups

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Abstract—Fifteen *p*-terphenyls containing alkoxylated backbones with and without cyano groups on the phenyl moieties have been designed and synthesized. The influences of the position and the number of cyano groups on the phenyl moieties as well as the skeleton to the absorption and emission spectra both, in solution and in solid state of these new *p*-terphenyls are discussed.

1. Introduction

Recently, we have reported a series of distyrylbenzene (DSB) derivatives, as the oligomeric analogue of poly-*para*-phenylene-vinylene (PPV), which was assessed as the emitter in organic light emitting diode (OLED) fabrication.[1] The presence of electron-withdrawing cyano group at various positions in the molecule may influence on the photophysical property and the electroluminescent behavior of these derivatives in OLED. Thus, bright blue emissions were achieved with these materials, as a dopant, in the device structure of ITO/NPB/CBP/TPBI:DSB/TPBI/Mg:Ag.[1] Although there were not much difference in the absorption and emission spectra of the analogues compounds containing *n*-hexyloxy and 2-ethylhexyloxy groups. However, 2-ethylhexyloxy groups could produce more saturated blue color in their EL. Our preliminary results from ZINDO calculations[2] on *p*-terphenyls with or without cyano groups on the phenylene moieties showed that *para*- or *meta*-substituted cyano groups on the peripheral rings could cause red shifts in the absorption spectra. The presence of the alkoxy unit should enhance the solubility of oligomers and the introduction of high electron affinity of cyano groups to oligo-*para*-phenylene-vinylene (OPV) derivatives has been reported to lower the energy of the LUMO and reduces the barrier to the electron injection in LED.[3] Thus, PPV derivatives containing cyano groups could present high electron affinity and therefore exhibit a relatively low threshold voltage and high quantum efficiency in LED devices even using stable aluminum electrodes.[4] However, despite its interesting properties in this field, as to our knowledge, there is no report in the literature about the synthesis of the *p*-terphenyls with or without cyano groups on the phenylene moieties. The aryl–aryl bond formation has been known for more than a century and was one of the first reaction using a transition metal.[5] Over the last ten years many articles have dealt with new results in the area of aryl–aryl bond formation. Nowadays, many more syntheses use palladium catalysts than their nickel and copper counterparts. As to our knowledge, the palladium-catalyzed Stille,[6] Suzuki,[7] Negishi,[8] and Kumada[9] reaction have been the most studied over the past few years. We have focused on the Suzuki coupling, a palladium(0)-catalyzed carbon–carbon bond-forming reaction between an organohalide and an organoboron reagent, in the α-arylation or α-vinylation of *N*,*N*-dimethylacetamide recently.[10,11] Since the boron reagents are compatible with a large number of functional groups and tolerate cyanides, thus fulfilling our goals for synthetic flexibility. Herein, we report the efficient synthesis of a series of *p*-terphenyl with and without cyano groups **1**–**10** and their photoluminescent behavior. As for comparison, we also synthesized *p*-terphenyl derivatives with cyano groups on the central benzene ring and *p*-terphenyl with hexahexyloxyl groups **11**–**15** (Scheme 1).

2. Results and discussion

The Suzuki cross-coupling reaction to form *p*-terphenyls with or without cyano groups were shown in Scheme 1. Thus, the palladium-catalyzed cross-coupling reaction of

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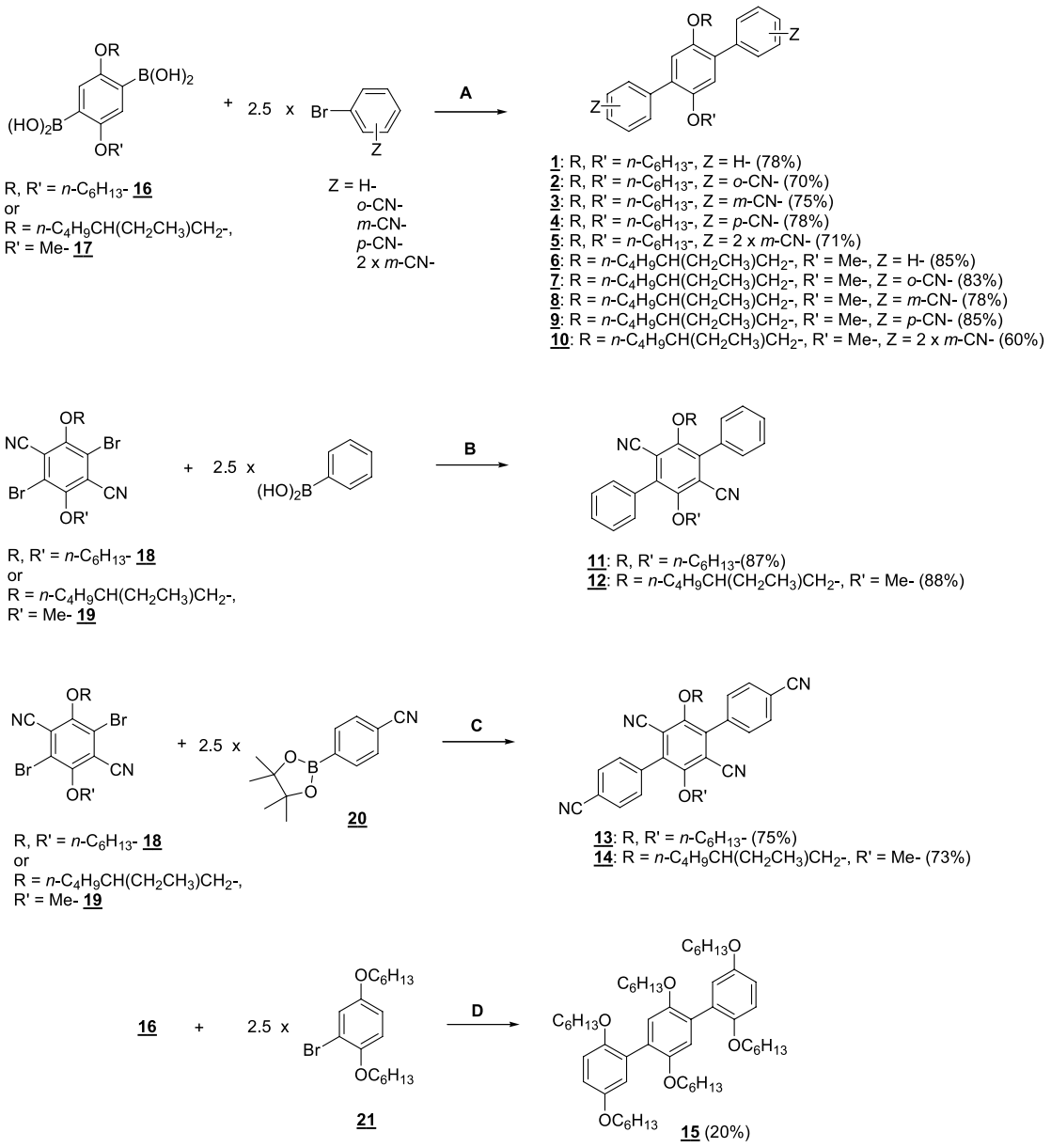

Scheme 1. Synthesis of a series of *p*-terphenyl with or without cyano groups.

2,5-dihexyloxy-1,4-benzenediboronic acid (**16**), prepared in 79% yield from the lithium–halogen exchange reaction of 2,5-dibromo-1,4-dihexyloxybenzene with *n*-butyllithium followed by the treatment of trimethylborate and dilute acid, with 2.5 equiv of bromoarene with or without cyano groups at *ortho*-, *meta*-, *para*-, or two *meta*-positions in the presence K_2CO_3 as the base in DMSO could give *p*-terphenyls **1**–**5** in fair to good yields (70 to 78%). Under the similar reaction conditions, the cross-coupling reaction of 2,5-dibromo-1,4-dihexyloxybenzene with arylboronic acid with or without cyano groups gave **1**–**5** in low yields (33 to 42%). Likewise, 2-(2-ethylhexyloxy)-5-methoxy-1,4-benzenediboronic acid (**17**) could give the corresponding *p*-terphenyls **6**–**10** in fair to good yields (60 to 85%). 2,5-Dibromo-3,6-dihexyloxybenzene-1,4-dicarbonitrile (**18**) and 2,5-dibromo-6-(2-ethylhexyloxy)-3-methoxybenzene-1,4-dicarbonitrile (**19**) could undergo Suzuki coupling reaction with 2.5 equiv of phenylboronic acid to give *p*-terphenyls **11** and **12** with cyano groups on the central benzene ring in 87 and 88% yields, respectively. The coupling of **18** and **19** with phenylboronic acid with cyano groups on the phenyl rings, prepared from lithium–halogen exchange of cyano-substituted bromobenzene and *n*-butyllithium at −78 °C in THF followed by the addition of trimethylborate, gave very low yields. However, the palladium-catalyzed cross-coupling reaction of 2.5 equiv of 4,4,5,5-tetramethyl-2-(4-cyanophenyl)-1,3,2-dioxaborolane (**20**) with **18** and **19** could give *p*-terphenyls **13**–**14** with two cyano groups on the central benzene ring and two cyano groups at the *para*-positions of the peripheral rings in 75 and 73% yields, respectively. The use of $PdCl_2$(dppf) as the catalyst and K_3PO_4 as the base could give better yields than

Table 1. UV spectral data of symmetric and asymmetric *p*-terphenyls

Compound	UV[a] λ_{max} (nm)	UV[b] λ_{max} (nm)	$\varepsilon^{a}\times10^{3}$ dm^{3} mol^{-1} cm^{-1}
1	320	357	7.96
2	331	372	2.20
3	332	337	7.55
4	346	383	8.81
5	344	361	7.98
6	318	320	10.22
7	327	335	9.38
8	329	346	12.32
9	342	368	9.62
10	345	356	8.96
11	341	355	9.61
12	336	349	6.61
13	337	347	11.95
14	336	347	8.88

[a] The UV spectra in ethyl acetate solution.
[b] The UV spectra in solid state.

the use of other kinds of catalysts ($Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$) and bases (K_2CO_3, CsF, Cs_2CO_3, *i*-Pr_2NEt) in the case of coupling 1,3,2-dioxaborolane with **18** and **19**. Attempts to prepare 3,6-dicyano-2,5-dihexyloxy-1,4-benzenediboronic acid from **18** by lithium–halogen exchange at low temperature and followed by the addition of trimethylborate gave only debrominated product, 2,5-dihexyloxybenzene-1,4-dicarbonitrile, in 70% yield. The palladium-catalyzed cross-coupling reaction of **16** with 2.5 equiv of 2-bromo-1,4-dihexyloxy-benzene (**21**), prepared in 86% yield by mono-lithium–halogen exchange of 2,5-dibromo-1,4-dihexyloxybenzene with *n*-butyllithium followed by acidic hydrolysis, gave *p*-terphenyl **15** with hexahexyloxyl groups. Attempts to couple **16** with 4-bromo-2,5-dihexyloxybenzenecarbonitrile in the presence of various palladium catalysts and bases failed.

Tables 1 and 2 showed the λ_{max} of their UV, PL, and EX spectral data along with the extinction coefficiency and the fluorescent quantum yield, Φ_F, of *p*-terphenyls **1**–**14** both in ethyl acetate solution and in their solid states. In general, the extinction coefficiencies of UV spectra in solution for *p*-terphenyls without cyano groups on the central benzene ring (**1**–**10**) are higher for asymmetric *p*-terphenyls (**6**–**10**) containing 2-ethylhexyloxy and methoxy groups than the corresponding symmetric *p*-terphenyls (**1**–**5**) containing two *n*-hexyloxy groups. The lower extinction coefficiency (a measure of transition probability or allowedness of an electronic transition at a given wavelength) for **1**–**5** may be due to their bigger steric hindrance than that for the corresponding **6**–**10**.[12] Since one of the *n*-hexyloxy group in **1**–**5** is a little bigger than the corresponding methoxy group in **6**–**10** so that the three phenyl groups tend to be non-coplanar in **1**–**5**, while the three phenyl groups are relatively not so non-coplanar in **6**–**10**.[13] That means that there is a bigger structure change in the excited states from the ground states for **1**–**5** than that for **6**–**10**. So, the transition probability for **6**–**10** is higher than that of **1**–**5**. In other words, the extinction coefficiencies for **6**–**10** is relatively higher than that for **1**–**5**. On the contrary, the extinction coefficiencies of UV spectra for *p*-terphenyls with cyano groups on the central benzene ring (**11**–**14**) is lower for asymmetric *p*-terphenyls (**12** and **14**) than the corresponding symmetric *p*-terphenyls (**11** and **13**). For *p*-terphenyls **1**–**14**, the λ_{max} in both UV absorption and PL emission spectra in solution shows a red shift (2 to 6 nm) for symmetric

Table 2. PL and EX spectral data of symmetric and asymmetric *p*-terphenyls

Compound	PL[a] λ_{max} (nm)	PL[b] λ_{max} (nm)	EX[a] λ_{max} (nm)	EX[b] λ_{max} (nm)	Φ_F [a,c]
1	385	384	319 277	329 283	0.530
2	413	403	330 274	344 244	0.513
3	402	411	331 278	332 268	0.573
4	424	420	344 290	358 294	0.834
5	419	452	347 280	351 281	0.867
6	381	397	321 277	323 281	0.571
7	408	401	328 276	344 259	0.560
8	399	415	333 279	344 270	0.616
9	420	418	344 288	360 291	0.921
10	422	448	341 280	353 284	0.823
11	419	402	338 278	348 265	0.159
12	413	394	337 279	344 284	0.183
13	431	409	339 279	342 268	0.210
14	430	408	335 277	339 259	0.231

[a] In ethyl acetate.
[b] In solid state.
[c] Use Coumarin I in ethyl acetate (Φ_F=0.99) as the standard.[15]

p-terphenyls than asymmetric *p*-terphenyls except the pair of **5** and **10**. Symmetric *p*-terphenyl **5** with four cyano groups at *meta*-positions on the peripheral rings has a blue shift (1 and 3 nm in UV and PL spectra, respectively), than the corresponding asymmetric *p*-terphenyl **10**. The fluorescence quantum yield for symmetric and asymmetric *p*-terphenyls with cyano groups at either *para*-positions or two *meta*-positions on the peripheral rings are much higher than that of other *p*-terphenyls. The results also showed that the fluorescence quantum yields decreased when cyano groups are substituted on the central benzene ring (**11**–**14**). All the excitation spectra of these *p*-terphenyls showed two electronic transitions. Such behavior points to a strong mesomeric interaction of the alkoxy groups with the terphenyl chromophore.[14]

The λ_{max} in both UV absorption and PL emission spectra for **15** with hexahexyloxyl groups (319 and 385 nm, respectively), are similar to that of symmetric *p*-terphenyl **1** and asymmetric *p*-terphenyl **6** with only two alkoxy groups on the central benzene ring. This indicated that alkoxy group influenced very little on the λ_{max} in both absorption and emission spectra.

It is interesting to know that the λ_{max} in UV of these symmetric and asymmetric *p*-terphenyls shows a red shift in solid state than that in ethyl acetate solution, especially for symmetric *p*-terphenyls **1**, **2**, and **4**, which could have 37–41 nm red shift in their solid states than that in ethyl acetate solution. Furthermore, symmetric *p*-terphenyls **1** and **2** both have a red shift (37 nm) in absorption than the corresponding asymmetric *p*-terphenyls **6** and **7** in their solid states. Contrast to the λ_{max} in UV of these symmetric and asymmetric *p*-terphenyls, only symmetric and asymmetric *p*-terphenyls with two or four cyano groups at the *meta*-positions of the peripheral rings (**3**, **5**, **8**, and **10**) showed a red shift (9–33 nm) of the emission spectra in their solid states than that in ethyl acetate solution, other symmetric and asymmetric *p*-terphenyls showed a blue shift (1–22 nm) in the emission of their solid states than that in ethyl acetate solution. Thus, the solid state of symmetric and asymmetric *p*-terphenyls with four cyano groups at the *meta*-positions of the peripheral rings could reach to the blue light range in PL spectra. The preparation of devices and their electro-optical properties are still under active investigation in our collaborator's lab, and their results will be reported elsewhere when they are available.

3. Conclusion

Fifteen alkoxylated *p*-terphenyls with or without cyano groups on either the central benzene ring or the peripheral rings have been synthesized efficiently. The extinction coefficiencies of UV spectra for *p*-terphenyls without cyano groups on the central benzene ring are higher for asymmetric *p*-terphenyls than the corresponding symmetric *p*-terphenyls. The fluorescence quantum yield for *p*-terphenyls with cyano groups at either *para*-positions or two *meta*-positions of the peripheral rings are much higher than that of other *p*-terphenyls. The fluorescence quantum yields decreased when cyano groups are substituted on the central benzene ring. Alkoxy group influenced very little on the λ_{max} in both UV absorption and PL emission spectra. The λ_{max} in UV of these *p*-terphenyls shows a red shift in solid state than that in solution. Furthermore, only *p*-terphenyls with two or four cyano groups at the *meta*-positions of the peripheral rings showed a red shift in emission spectra in their solid states than that in solution, other *p*-terphenyls showed a blue shift in the emission spectra in their solid states. The relationship between the position and number of cyano groups and their influence on the absorption and emission spectra of these *p*-terphenyls is very interesting as compared to the phenylene–vinylene analogues and need to have further studied.

4. Experimental

4.1. General

4.1.1. Representative procedure of Suzuki coupling reaction for the preparation of 2,5-dihexyloxy-1,4-diphenylbenzene (1). *o*-Xylene (25 mL) was added to a mixture of 2,5-dihexyloxy-1,4-benzenediboronic acid (2.20 g, 5 mmol), bromobenzene (1.95 g, 12.5 mmol), and potassium carbonate (4.15 g, 30 mmol) in a 100 mL round-bottom flask under nitrogen atmosphere. A solution of $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol) in 5 mL of *o*-xylene was added into the above mixture at 130 °C. The mixture was cooled to room temperature after it was stirred and heated for 72 h. The mixture was worked up with water and ethyl acetate. The organic layer was dried over magnesium sulfate, filtrated, and concentrated before recrystallization by ethyl acetate and methanol to give 1.81 g (83% yield) of the desired product. Mp 67–68 °C; R_f=0.9 (*n*-hexane/ethyl acetate=4:1) ; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, J=7 Hz, 6H), 1.26–1.36 (m, 12H), 1.65–1.68 (m, 4H), 3.90 (t, J=6.4 Hz, 4H), 6.98 (s, 2H), 7.32 (t, J=7.5 Hz, 2H), 7.41 (t, J=7.5 Hz, 4H), 7.60 (d, J=7.5 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.96, 22.56, 25.72, 29.33, 31.45, 69.70, 116.44, 126.88, 127.89, 129.53, 130.91, 138.46, 150.31 ppm; IR ν 1484.8, 1400.4, 1211.4, 1054.1, 763.9, 698.1 cm^{-1}; MS *m*/*z* 430 (M^+), 347, 262; HRMS calcd for $C_{30}H_{38}O_2$: 430.2872; found: 430.2869. Anal. Calcd for $C_{30}H_{38}O_2$: C, 83.68; H, 8.89. Found: C, 83.82; H, 8.79.

4.1.2. 2-[4-(2-Cyanophenyl)-2,5-dihexyloxyphenyl]benzenecarbonitrile (2). Mp 129–130 °C; R_f=0.6 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83 (t, J=7 Hz, 6H), 1.21–1.28 (m, 12H), 1.64–1.67 (m, 4H), 3.94 (t, J=6.5 Hz, 4H), 6.94 (s, 2H), 7.44 (t, J=7.6 Hz, 2H), 7.56 (d, J=7.7 Hz, 2H), 7.64 (t, J=7.7 Hz, 2H), 7.74 (d, J=7.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.88, 22.47, 25.53, 29.05, 31.35, 69.19, 113.21, 115.51, 118.61, 127.42, 128.52, 131.11, 132.17, 132.74, 142.17, 149.80 ppm; IR ν 2228.1, 1513.9, 1390.7, 1215.4, 1035.9, 762.8 cm^{-1}; MS *m*/*z* 480.2 (M^+), 412.0, 395.2, 313.1; HRMS calcd for $C_{32}H_{36}O_2N_2$: 480.2777; found: 480.2786. Anal. Calcd for $C_{32}H_{36}O_2N_2$: C, 79.97; H, 7.55; N, 5.83. Found: C, 79.75; H, 7.67; N, 5.72.

4.1.3. 3-[4-(3-Cyanophenyl)-2,5-dihexyloxyphenyl]benzenecarbonitrile (3). Mp 102–103 °C; R_f=0.525 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, J=7.5 Hz, 6H), 1.26–1.68 (m, 12H),

1.67–1.71 (m, 4H), 3.94 (t, J=6 Hz, 4H), 6.94 (s, 2H), 7.52 (t, J=7.7 Hz, 2H), 7.63 (d, J=7.7 Hz, 2H), 7.7 (d, J=7.7 Hz, 2H), 7.89 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.96, 22.53, 25.75, 29.17, 31.40, 69.58, 112.21, 115.48, 118.93, 128.77, 129.21, 130.57, 133.14, 133.89, 139.29, 150.16 ppm; IR ν 2232.1, 1478.3, 1397.7, 1216.6, 1037.7, 785.9 cm^{-1}; MS m/z 480.2 (M^+), 397.1, 325.1, 312.1; HRMS calcd for $C_{32}H_{36}O_2N_2$: 480.2777; found: 480.2772. Anal. Calcd for $C_{32}H_{36}O_2N_2$: C, 79.97; H, 7.55; N, 5.83. Found: C, 79.76; H, 7.73; N, 5.97.

4.1.4. 4-[4-(4-Cyanophenyl)-2,5-dihexyloxyphenyl]benzenecarbonitrile (4). Mp 153–154 °C; R_f=0.68 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, J=7 Hz, 6H), 1.25–1.33 (m, 12H), 1.67–1.68 (m, 4H), 3.93 (t, J=6 Hz, 4H), 6.93 (s, 2H), 7.69 (s, 8H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.89, 22.48, 25.65, 29.11, 31.31, 69.56, 110.70, 115.55, 118.96, 129.82, 130.13, 131.70, 142.80, 150.18 ppm; IR ν 2226.4, 1647.6, 1601.0, 1214.5, 776.0 cm^{-1}; MS m/z 480.2 (M^+), 397.1, 325.1, 312.1; HRMS calcd for $C_{32}H_{36}O_2N_2$: 480.2777; found: 480.2772. Anal. Calcd for $C_{32}H_{36}O_2N_2$: C, 79.97; H, 7.55; N, 5.83. Found: C, 79.82; H, 7.75; N, 5.94.

4.1.5. 1,4-Bis(3,5-dicyanophenyl)-2,5-dihexyloxybenzene (5). Mp 214–215 °C (dec); R_f=0.75 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, J=7.0 Hz, 6H), 1.28–1.36 (m, 12H), 1.69–1.72 (m, 4H), 3.97 (t, J=6.4 Hz, 4H), 6.91 (s, 2H), 7.90 (s, 2H), 8.08 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.93, 22.48, 25.79, 29.02, 31.35, 69.56, 113.88, 114.72, 116.67, 127.60, 133.47, 136.83, 140.50, 150.06 ppm; IR ν 2236.2, 1222.1, 1026.7, 871.8, 779.72, 676.5 cm^{-1}; MS m/z 530.1 (M^+) 443.1, 389.1, 362.0, 273.1; HRMS calcd for $C_{34}H_{34}O_2N_4$: 530.2682; found: 530.2688.

4.1.6. 2-(2-Ethylhexyloxy)-5-methoxy-1,4-diphenylbenzene (6). R_f=0.86 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82–0.88 (m, 6H), 1.23–1.38 (m, 8H), 1.60–1.64 (m, 1H), 3.79–3.83 (m, 5H), 6.99–7.01 (m, 2H), 7.34–7.36 (m, 2H), 7.41–7.47 (m, 4H), 7.60–7.62 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.07, 14.02, 23.00, 23.89, 30.54, 39.57, 56.42, 71.80, 114.64, 116.14, 126.89, 127.05, 127.81, 128.06, 129.46, 129.58, 130.39, 130.89, 138.39, 150.45, 150.55 ppm; IR ν 1600.1, 1519.9, 1393.4, 1208.3,1057.1, 760.2 cm^{-1}; MS m/z 388.2 (M^+), 289.1, 276.1, 262.1, 215; HRMS calcd for $C_{27}H_{32}O_2$: 388.2402; found: 388.2403.

4.1.7. 2-[4-(2-Cyanophenyl)-2-(2-ethylhexyloxy)-5-methoxyphenyl]benzenecarbonitrile (7). Mp 148–149 °C; R_f=0.38 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76–0.89 (m, 6H), 1.14–1.24 (m, 8H), 1.60–1.62 (m, 1H), 3.79–3.81 (m, 5H), 6.91 (s, 1H), 6.94 (s, 1H), 7.42–7.43 (m, 2H), 7.53–7.55 (m, 2H), 7.61–7.65 (m, 2H), 7.73–7.75 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.04, 13.94, 22.91, 23.81, 28.89, 30.47, 39.38, 56.11, 71.58, 113.12, 113.26, 114.27, 115.49, 118.55, 118.58, 127.48, 127.54, 128.18, 128.65, 130.96, 131.14, 132.06, 132.42, 132.67, 132.88, 142.01, 142.13, 150.12 ppm; IR ν 2228.8, 1472.8, 1395.4, 1214.7, 1037.8, 757.6 cm^{-1}; MS m/z 438.1 (M^+), 327.1, 326.1, 311.1, 295.1; HRMS calcd for $C_{29}H_{30}O_2N_2$: 438.2307; found: 438.2309. Anal. Calcd for $C_{29}H_{30}O_2N_2$: C, 79.42; H, 6.89; N, 6.39. Found: C, 79.63; H, 7.05; N 6.54.

4.1.8. 3-[4-(3-Cyanophenyl)-2-(2-ethylhexyloxy)-5-methoxyphenyl]benzenecarbonitrile (8). Mp 89–90 °C; R_f=0.48 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81–0.85 (m, 6H), 1.21–1.35 (m, 8H), 1.60–1.62 (m, 1H), 3.78–3.83 (m, 5H), 6.92 (s, 1H), 6.93 (s, 1H), 7.50–7.54 (m, 2H), 7.61–7.63 (m, 2H), 7.79–7.81 (m, 2H), 7.87–7.88 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.06, 13.97, 22.92, 23.93, 28.97, 30.60, 39.49, 56.33, 71.74, 112.12, 11.29, 114.00, 115.33, 118.84, 118.94, 128.70, 128.90, 130.56, 130.63, 133.07, 133.18, 133.82, 133.88, 132.67, 132.88, 142.01, 139.19, 150.37, 150.43 ppm; IR ν 2228.0, 11518.3, 1396.4, 1216.1, 1039.0, 680.1 cm^{-1}; MS m/z 439.1 (M^++1), 326.1, 265.1, 190.1; HRMS calcd for $C_{29}H_{31}O_2N_2$: 439.2386; found: 439.2389. Anal. Calcd for $C_{29}H_{30}O_2N_2$: C, 79.42; H, 6.89; N, 6.39. Found: C, 79.66; H, 6.76; N, 6.31.

4.1.9. 4-[4-(4-Cyanophenyl)-2-(2-ethylhexyloxy)-5-methoxyphenyl]benzenecarbonitrile (9). Mp 192–193 °C; R_f=0.13 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80–0.84 (m, 6H), 1.20–1.33 (m, 8H), 1.55–1.57 (m, 1H), 3.79–3.81 (m, 5H), 6.93 (s, 1H), 6.94 (s, 1H), 7.66–7.71 (m, 8H) ppm; ^{13}C NMR($CDCl_3$,125 MHz) δ 11.05, 13.96, 22.92, 23.90, 28.92, 30.54, 39.48, 56.35, 71.71, 110.74, 110.84, 114.14, 115.38, 118.97, 129.51, 129.84, 130.11, 130.19, 131.65, 131.86,142.70, 142.79, 150.44, 150.47 ppm; IR ν 2228.8, 1601.8, 1211.1, 1048.8, 846.1, 554.8 cm^{-1}; MS m/z 439.2 (M^++1), 339.1, 326.1, 267.1; HRMS calcd for $C_{29}H_{31}O_2N_2$: 439.2386; found: 439.2388. Anal. Calcd for $C_{29}H_{30}O_2N_2$: C, 79.42; H, 6.89; N, 6.39. Found: C, 79.56; H, 6.97; N, 6.66.

4.1.10. 1,4-Bis(3,5-dicyanophenyl)-2-(2-ethylhexyloxy)-5-methoxybenzene (10). Mp >300 °C; R_f=0.575 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83–0.87 (m, 6H), 1.20–1.38 (m, 8H), 1.60–1.68 (m, 1H), 3.84–3.87 (m, 5H), 6.91 (s, 1H), 6.92 (s, 1H), 7.90 (s, 2H), 8.06 (s, 2H), 8.08 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.11, 14.03, 22.94, 24.02, 29.05, 30.72, 39.47, 56.39, 71.86, 113.55, 113.91, 114.03, 114.77, 116.64, 116.78, 133.54, 133.60, 136.87, 136.91, 140.74, 150.38 ppm; IR ν 2237.7, 1593.0, 1388.2, 1218.4, 1028.8, 875.6 cm^{-1}; MS m/z 488.1 (M^+) 460.0, 443.1, 338.3, 195.1; HRMS calcd for $C_{31}H_{28}O_2N_4$: 488.2212; found: 488.2212.

4.1.11. 3,6-Dihexyloxy-2,5-diphenylbenzene-1,4-dicarbonitrile (11). Mp 134–135 °C; R_f=0.77 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (t, J=7 Hz, 6H), 1.08–1.20 (m, 12H), 1.47–1.49 (m, 4H), 3.62 (t, J=7 Hz, 4H), 7.52 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.89, 22.38, 25.09, 29.65, 31.20, 75.54, 113.78, 114.32, 128.58, 129.36, 129.61, 132.44, 139.47, 155.67 ppm; IR ν 2226.8, 1660.0, 1217.3, 763.9, 667.9 cm^{-1}; MS m/z 481.2 (M^++1), 397.2, 325.5, 312.1; HRMS calcd for $C_{32}H_{37}O_2N_2$: 481.2855; found: 481.2852. Anal. Calcd for $C_{32}H_{36}O_2N_2$: C, 79.97; H, 7.55; N, 5.83. Found: C, 79.80; H, 7.65; N, 5.98.

4.1.12. 6-(2-Ethylhexyloxy)-3-methoxy-2,5-diphenylbenzene-1,4-dicarbonitrile (12). Mp 132–133 °C; R_f=0.7

(*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (t, J=7.4 Hz, 3H), 0.82 (t, J=7.5 Hz, 3H), 1.01–1.23 (m, 8H), 1.34–1.39 (m, 1H), 3.54–3.55 (m, 5H), 7.48–7.55 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.84, 13.95, 22.80, 23.21, 28.80, 29.82, 40.17, 61.98, 78.01, 113.50, 114.19, 128.61, 129.73, 129.46, 129.64, 139.23, 139.65, 156.03, 156.11 ppm; IR ν 2231.7, 1444.2, 1378.5, 1240.2, 1010.5, 699.2 cm^{-1}; MS *m*/*z* 438.2 (M^+), 326.1, 311.1, 282.1, 256.1, 227.1; HRMS calcd for $C_{29}H_{30}O_2N_2$: 438.2307; found: 438.2299. Anal. Calcd for $C_{29}H_{30}O_2N_2$: C, 79.42; H, 6.89; N, 6.39. Found: C, 79.58; H, 6.97; N, 6.55.

4.1.13. 1,4-Bis(4-cyanophenyl)-3,6-dicyano-2,5-dihexyloxybenzene (13). Mp 112–113 °C; R_f=0.36 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (t, J=7.3 Hz, 6H), 1.08–1.23 (m, 12H), 1.46–1.49 (m, 4H), 3.66 (t, J=6.4 Hz, 4H), 7.62 (d, J=8.3 Hz, 4H), 7.82 (d, J=8.3 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.92, 22.43, 25.13, 29.70, 31.20, 76.00, 113.56, 113.64, 113.78, 117.97, 130.60, 132.45, 136.71, 138.65, 155.67 ppm; IR ν 2236.2, 1435.9, 1373.3, 1306.9, 1218.4, 997.2, 757.6 cm^{-1}; MS *m*/*z* 530.1 (M^+), 443.1, 389.1, 362.0, 273.1; HRMS calcd for $C_{34}H_{34}O_2N_4$: 530.2682; found: 530.2686. Anal. Calcd for $C_{34}H_{34}O_2N_4$: C, 76.96; H, 6.46; N, 10.56. Found: C, 77.10; H, 6.65; N, 10.59.

4.1.14. 1,4-Bis(4-cyanophenyl)-3,6-dicyano-2-(2-ethylhexyloxy)-5-methoxybenzene (14). Mp 194–195 °C; R_f=0.3 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.68 (t, J=7.5 Hz, 3H), 0.84 (t, J=7.5 Hz, 3H), 1.00–1.25 (m, 8H), 1.35–1.38 (m, 1H), 3.56–3.62 (m, 5H), 7.63–7.66 (m, 4H), 7.84–7.89 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.87, 13.99, 22.83, 23.21, 24.85, 28.86, 29.83, 40.27, 62.55, 78.85, 113.37, 113.49, 113.56, 113.81, 113.88, 117.92, 130.43, 130.65, 132.44, 132.60, 135.09, 136.49, 136.66, 138.50, 138.77, 156.00, 156.09 ppm; IR ν 2231.1, 1376.5, 1101.4, 836.3, 558.5 cm^{-1}; MS *m*/*z* 489.1 (M^++1) 388.1, 376.0, 349.1, 263.1; HRMS calcd for $C_{31}H_{29}O_2N_4$: 489.2391; found: 489.2305. Anal. Calcd for $C_{31}H_{28}O_2N_4$: C, 76.21; H, 5.78; N, 11.47. Found: C, 76.42; H, 5.88; N, 11.62.

4.1.15. 2-[4-(2,5-Dihexyloxyphenyl)-2,5-dihexyloxyphenyl]-1,4-dihexyloxybenzene (15). Mp 64–65 °C (dec); R_f=0.9 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83–0.92 (m, 18H), 1.22–1.34 (m, 24H), 1.56–1.64 (m, 12H), 1.75–1.78 (m, 12H), 3.81–3.94 (m, 12H), 6.81–702 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.98, 22.55, 25.65, 25.68, 25.74, 29.39, 29.65, 31.56, 31.59, 68.55, 69.41, 69.47, 69.70, 114.07, 114.39, 116.72, 116.88, 117.06, 117.99, 127.44, 127.54, 129.35, 149.95, 150.00, 150.75, 152.74 ppm; MS *m*/*z* 830 (M^+), 630, 570, 554, 486, 470; IR ν 1465.4, 1207.4, 1037.8, 938.2, 798.2 cm^{-1}; HRMS calcd for $C_{54}H_{86}O_6$: 830.6424; found: 830.6425.

4.1.16. 2,5-Dihexyloxy-1,4-benzenediboronic acid (16). *n*-Butyllithium (2.5 M in hexanes, 5 mL, 12.5 mmol) was added dropwise to a solution of 2,5-dibromo-1,4-dihexyloxybenzene (2.2 g, 5 mmol) in dried diethyl ether (50 mL) for 1 h at 0 °C followed by the dropwise addition of trimethylborate (1.7 mL, 15 mmol). The mixture was gradually warmed up and stirred for another 12 h. Then, 2 N HCl (20 mL) was added and stirred for another 30 min before adding water (30 mL). The product was extracted by diethyl ether (50 mL×5), dried over magnesium sulfate, filtrated, and concentrated. Ethyl acetate (60 mL) was added to the concentrated mixture, filtrated and used ethyl acetate to washed the precipitate. After removing volatile solvents under vacuum, the product was obtained as a white powder (2.27 g, 79% yield). Mp 194–195 °C (dec); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.93 (t, J=7 Hz, 6H), 1.34–1.48 (m, 12H), 1.76–1.80 (m, 4H), 3.36 (s, 4H), 4.04 (t, J=6.5 Hz, 4H), 7.83 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.24, 22.42, 25.52, 29.14, 31.33, 68.82, 118.39, 124.87 (*C*–B(OH)$_2$), 157.31 ppm.

4.1.17. 2-(2-Ethylhexyloxy)-5-methoxy-1,4-benzenediboronic acid (17). Following the procedure as described above for the synthesis of **16**, compound **17** was prepared from 1,4-dibromo-2-(2-ethyl-hexyloxy)-5-methoxybenzene (1.97 g, 5 mmol), *n*-butyllithium (2.5 M in hexanes, 5 mL, 12.5 mmol), and trimethylborate (1.42 mL, 12.5 mmol). The crude product (1.26 g, 78% yield) was used without further purification. It can be further purified by recrystallization three times from ethyl acetate to give the desired product **17** as a white solid. Mp 114–115 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.77 (t, J=7 Hz, 6H), 1.17–1.33 (m, 8H), 1.58 (m, 1H), 3.67 (s, 3H), 3.78 (d, J=5.5 Hz, 2H), 7.07 (s, 1H), 7.08 (s, 1H), 7.68 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 11.40, 14.34, 22.90, 23.89, 28.86, 30.45, 39.77, 56.17, 71.13, 117.18, 118.31, 124.68 (*C*–B(OH)$_2$), 125.18 (*C*–B(OH)$_2$), 157.48, 157.80 ppm.

4.1.18. 2,5-Dibromo-3,6-dihexyloxybenzene-1,4-dicarbonitrile (18). To a mixture of 2,5-dihexyloxybenzene-1,4-dicarbonitrile (1.65 g, 5 mmol) and *N*-bromosuccinimide (2.23 g, 12.5 mmol) in 100 mL round-bottom flask was added trifluoroacetic acid (2 mL) until all compounds are completely dissolved. Then, concentrated sulfuric acid (2.7 mL, 50 mmol) was added and stirred for another 4 h at room temperature. Saturated sodium bicarbonate (5 mL) was added to the mixture and extracted with ethyl acetate (30 mL×5), dried over magnesium sulfate, filtrated, and concentrated. The crude product was recrystallized by ethyl acetate (10 mL) and methanol (5 mL) to give 1.79 g (74% yield) of the desired product as a white powder. Mp 107–108 °C; R_f=0.775 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J=7 Hz, 6H), 1.32–1.54 (m, 12H), 1.83–1.93 (m, 4H), 4.16 (t, J=6.6 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.98, 22.50, 25.27, 29.94, 31.44, 76.75, 113.08, 117.00, 120.68, 156.43 ppm; IR ν 2234.0, 1427.9, 1371.9, 1204.4, 759.9 cm^{-1}; MS *m*/*z* 487.3 (M^++3), 484 (M^+), 219, 307, 370; HRMS calcd for $C_{20}H_{26}Br_2N_2O_2$: 484.0361; found: 484.0364. Anal. Calcd for $C_{20}H_{26}Br_2O_2N_2$: C, 49.40; H, 5.39; N, 5.76. Found: C, 49.62; H, 5.53; N, 5.89.

4.1.19. 2,5-Bibromo-6-(2-ethylhexyloxy)-3-methoxybenzene-1,4-dicarbonitrile (19). Following the procedure as described above for the synthesis of **18**, compound **19** was prepared from 2-(2-ethylhexyloxy)-5-methoxybenzene-1,4-dicarbonitrile (1.43 g, 5 mmol), *N*-bromosuccinimide (2.85 g, 15 mmol), trifluoroacetic acid (12 mL), and concentrated sulfuric acid (2.78 mL,

50 mmol). The crude product was recrystallized from ethyl acetate–methanol to give the desired product **19** as a white solid (1.95 g, 88% yield). Mp 125–126 °C; R_f=0.8 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.90–0.99 (m, 6H), 1.34–1.62 (m, 8H), 1.82–1.85 (m, 1H), 4.05–4.09 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.08, 14.02, 22.91, 23.43, 28.98, 29.93, 40.24, 62.70, 79.12, 112.83, 112.98, 116.70, 116.78, 120.55, 167.76, 156.80 ppm; IR ν 2233.4, 1455.1, 1376.9, 1208.9, 1007.2, 730.64 cm^{-1}; MS *m/z* 445 (M^++3), 442 (M^+), 334, 332, 316, 288; HRMS calcd for $C_{17}H_{21}Br_2N_2O_2$: 442.9970; found: 442.9966. Anal. Calcd for $C_{17}H_{20}Br_2N_2O_2$: C, 45.97; H, 4.54; N, 6.31. Found: C, 46.12; H, 4.69; N, 6.46.

4.1.20. 4,4,5,5-Tetramethyl-2-(4-cyanophenyl)-1,3,2-dioxaborolane (20). The mixture of 4-bromobenzenecarbonitrile (0.91 g, 5 mmol), potassium acetate (1.17 g, 15 mmol), bis(pinaconato)diboron (1.40 g, 5.5 mmol), $PdCl_2$(dppf) (0.018 g, 0.015 mmol) in DMSO (5 mL) was heated under nitrogen at 80 °C for 6 h. The mixture was cooled to room temperature and water (50 mL) was added, and the product was extracted with ethyl acetate (50 mL×3), dried over magnesium sulfate, filtrated, and concentrated. The product was purified by column chromatography (silica gel, ethyl acetate /*n*-hexanes=1/20) to give 0.86 g (75% yield) of the desired product. Mp 94–95 °C; R_f=0.725 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35 (s, 12H), 7.65 (d, J=7.7 Hz, 2H), 7.87 (d, J=7.7 Hz, 2H) ppm; IR ν 2221.4, 1358.5, 1273.7, 1441.0, 838.7, 650.7 cm^{-1}.

4.1.21. 2-Bromo-1,4-dihexyloxybenzene (21). To a solution of 2,5-dibromo-1,4-dihexyloxybenzene (2.2 g, 5 mmol) in dried diethyl ether (50 mL) at 0 °C was added *n*-butyllithium (2.5 M in hexanes, 2.2 mL, 5.5 mmol) dropwise. After the temperature of the mixture was gradually warmed up to the room temperature for 12 h, 2 N HCl (20 mL) was added to it and stirred for another 30 min. The product was extracted with ethyl acetate (50 mL×3), dried over magnesium sulfate, filtrated, and concentrated. The product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexanes=1/20) to give 1.45 g (80% yield) of the desired product as a liquid in orange color. R_f=0.85 (*n*-hexane/ethyl acetate=4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J=7 Hz, 6H), 1.22–1.56 (m, 12H), 1.70–1.83 (m, 4H), 3.78–4.07 (m, 4H), 6.81 (d, J=9.3 Hz, 2H), 7.10 (d, J=3.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.89, 22.49, 25.59, 29.15, 31.46, 68.50, 69.87, 112.58, 113.99, 114.34, 119.33, 149.61, 153.43 ppm; MS *m/z* 358.1, 356.1 (M^+), 278.2, 190.0; HRMS calcd for $C_{18}H_{29}BrO_2$: 356.1351; found: 356.1352.

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