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Novel 5-(oligofluorenyl)-1,10-phenanthroline type ligands: synthesis, linear and two-photon absorption properties

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Abstract

The synthesis and characterization of new 1,10-phenanthroline-based chromophores **LT1**, **LT2** and **LD1** featuring fluorene unit(s) are reported. Their absorption and emission as well as their two-photon absorption properties in the 450–650 nm spectral range are discussed in comparison with the parent 1,10-phenanthroline and already described ligands **L1** and **L2**.
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Keywords: 1,10-Phenanthroline type ligands; Two-photon absorption; Sonogashira reaction; Fluorenes

In the field of third-order nonlinear optics (NLO), organic materials were intensively studied over recent years[1] for their two-photon absorption (TPA) properties in view of several applications for optical power limiting,[2] three-dimensional optical data storage,[3] laser up-conversion,[4] microfabrication,[5] fluorescence imaging,[6] photodynamic therapy (PDT)[7] and photochemical delivery of biological messengers.[8] Recently, we published the spectroscopic properties (linear and TPA) of Ru complexes based on ligands **L1** and **L2**[9] (Fig. 1). This work highlighted the possibility of obtaining two-photon absorption in a broad wavelength range from 700 to 950 nm. This phenomenon is due to TPA in the intraligand charge transfer (ILCT) bands and the metal-ligand charge transfer bands (MLCT). Furthermore, the luminescence lifetime from the triplet MLCT state is several microseconds long.

These properties open the way to the TPEL (two-photon excited luminescence) phenomena, for example, in a

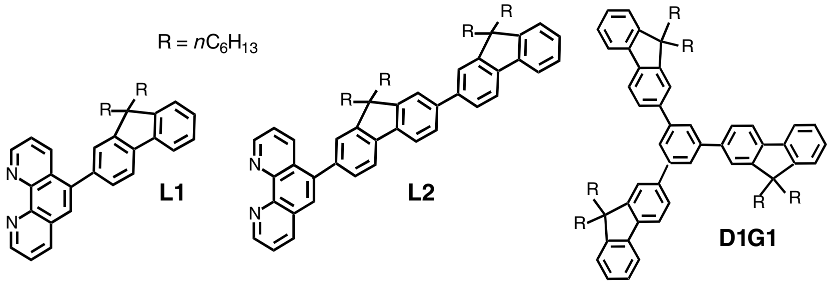

Fig. 1. Molecular structures of ligands **L1** and **L2** and of the octupole **D1G1**.

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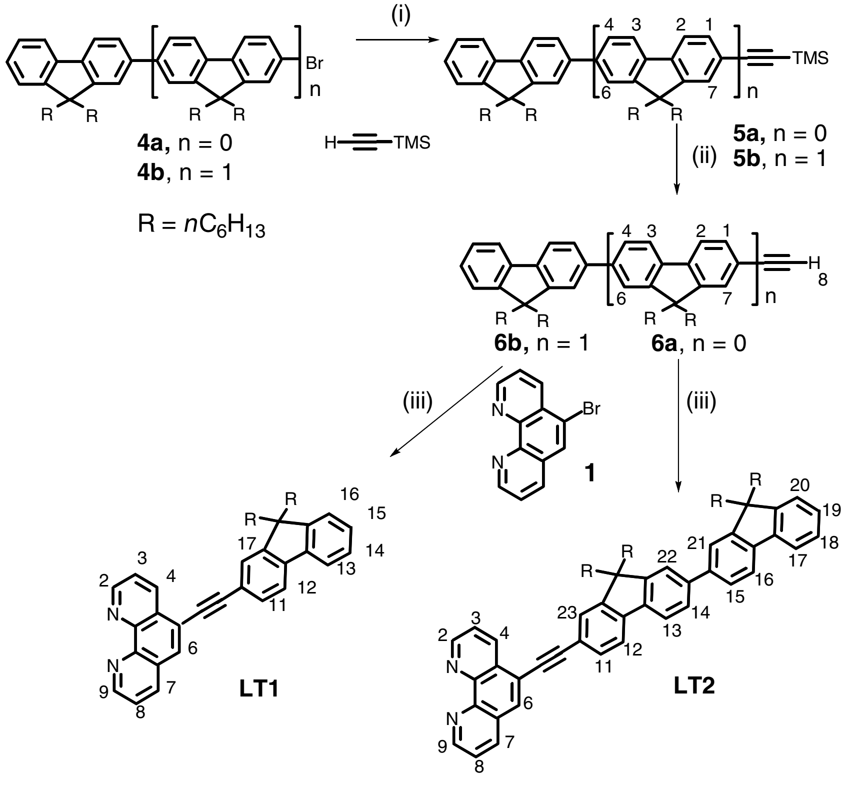
biological imaging purpose based on microsecond excited lifetimes, intermediate between the few ns of organic compounds[10] and the 100–2000 µs of europium(III) complexes.[11]

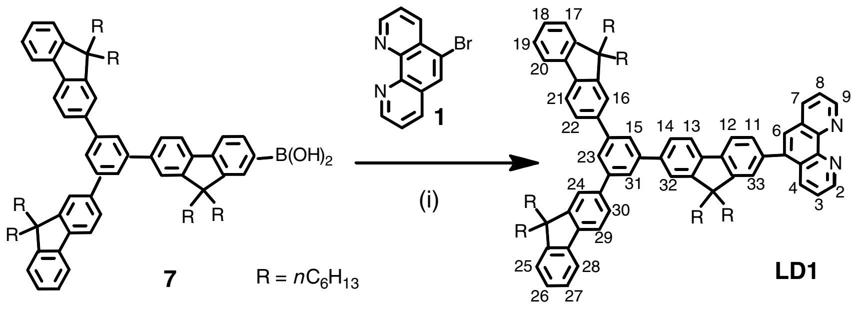
It may also concern applications involving further excited state reactivity (oxygen sensors,[12] PDT[13]), or excited state reabsorption such as optical power limiting, reported and discussed in the literature for organic or inorganic molecular materials[14] and dendron decorated Pt(II) complexes.[15]

To increase the TPA efficiency of Ru complexes from **L1** and **L2**, which led to very broad TPA properties from 500 to 950 nm,[9] we have designed new and more conjugated ligands **LT1**, **LT2** and **LD1**. We present in this Letter their synthesis and their spectroscopic characteristics (linear and TPA properties).

Synthesis of ligands **L1** and **L2,** represented in Figure 1, was based on a Suzuki cross-coupling reaction starting with the corresponding boronic acids[16] and 5-bromo-1,10-phenanthroline **1**.[17] Their analogs **LT1** and **LT2** (see Scheme 1), which possess a triple bond connecting the fluorene and polypyridyle moieties, were prepared using a Sonogashira reaction between **1** and the corresponding alkynes **6a** or **6b**. These alkynes were obtained as before from **4a** and **4b**, respectively, by a Sonogashira cross-coupling reaction with the trimethylsilane protected alkyne. Compounds were fully characterized by NMR and elementary analysis.[18] The preparation of compound **LD1** was achieved according to a Suzuki cross-coupling procedure (Scheme 2) starting from 5-bromo-1,10-phenanthroline **1** and the boronic compound **7**.[19]



Scheme 1. Reagents and conditions: (i) Pd(PPh$_3$)$_2$Cl$_2$, CuI, (iPr)$_3$N, reflux, 48 h (95% for **5a** and **5b**); (ii) K$_2$CO$_3$, MeOH, 24 h (88% for **6a** and 94% for **6b**); (iii) Pd(PPh$_3$)$_4$, pyrrolidine, 70 °C, 1 night (67% for **LT1** and 42% for **LT2**); general atom numbering also given for NMR description of **5a**, **6a**, **LT1** and **LT2**.



Scheme 2. Reagents and conditions: (i) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (1 M), toluene, reflux, 48 h (52%); general atom numbering also given for NMR description of **LD1**.

The UV–vis and luminescence spectra were recorded in chloroform. Absorption and emission spectra of these molecules are displayed in Figures 2 and 3, respectively. The spectra of **LT1** and **LT2** are shown in Figure 2a along with that of the phenanthroline for comparison. Similarly, the spectra of **LD1**, 1,10-phenanthroline and the octupole **D1G1** are shown in Figure 2b. The absorption spectra of **LT1** and **LT2** present a band at 280 and 275 nm, respectively. No solvatochromism effect was observed in spectroscopic properties for the three compounds, as shown for absorption of **LT1** in Supplementary data.

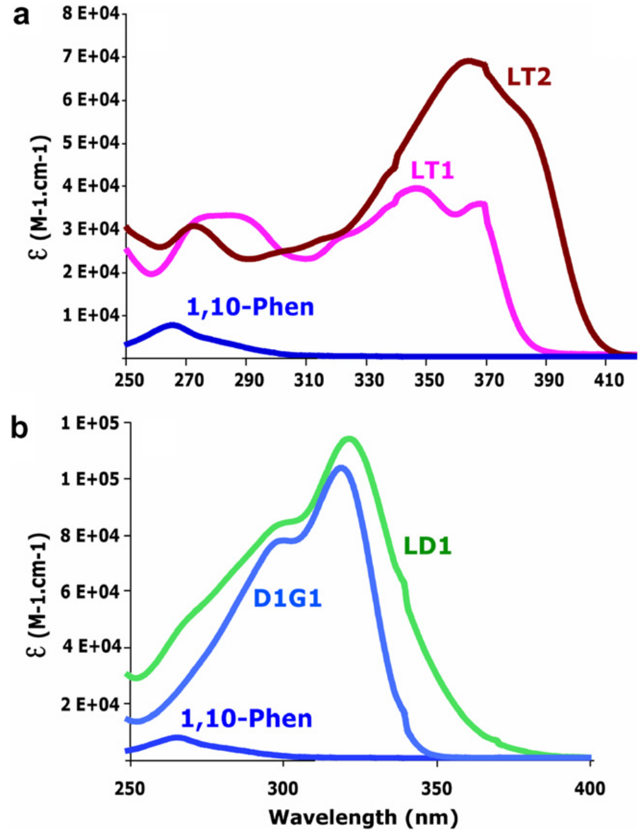


Fig. 2. (a) Absorption spectra measured in chloroform of **LT1**, **LT2** and (b) **LD1** compared with 1,10-phenanthroline.

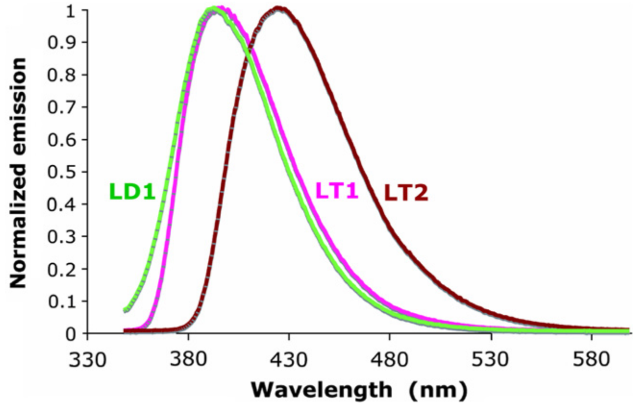


Fig. 3. Normalized emission spectra of **LD1**, **LT1** and **LD2** in diluted dichloromethane solution.

A similar band was already observed in **L1** and **L2** (at 270 and 265 nm, respectively) and ascribed mainly to the 1,10-phenanthroline according to semi-empirical calculations (see Ref. 9). Bands at 345 and 365 nm correspond to the ILCT bands from the oligofluorene to the phenanthroline moiety. These bands are red shifted with respect to those observed in **L1** and **L2** at 310 and 340 nm, respectively, as studied in our previous paper[9] (see Table 1). The absorption spectrum of **LD1** is similar to that of the octupole **D1G1** but revealing a weak shoulder at 270 nm attributed to the 1,10-phenanthroline.

As observed with absorption, the emission spectrum of **LT2** (see Fig. 3) is red shifted with respect to that of **LT1** (427 and 397 nm, respectively). The main characteristics (Stokes shift, quantum yields and fluorescence lifetimes) of these emissions are reported in Table 1 for **LT1**, **LT2** and **LD1**. These compounds possess high fluorescence quantum yields ($\geqslant 0.9$) and similar fluorescence lifetimes (1.3–1.6 ns). As far as **L1**, **L2** and **LT1**, **LT2** are compared,

Table 1
Photophysical characteristics of ligands **LT1**, **LT2** and **LD1** in comparison with **L1**, **L2** and **D1G1**

Compound	λ_{abs} (nm)	ε (L mol^{-1} cm^{-1})	λ_{em} (nm)/ λ_{exc} (nm)	Stokes shift (cm^{-1})	Φ	τ (ns)	λ_{TPA} (nm)	σ_{TPA} (GM)	Ref.
LT1	280, 345, 370	30,800, 34,400, 31,000	397/365	1990	1	1.6	460, 520, 570	140, 150, 100	This Work
LT2	275, 365	30,265, 68,515	427/375	3980	0.9	1.6	480, 520, 600	200, 350, 250	This Work
LD1	268, 300, 320	47,680, 82,770, 113,300	395/325	5680	0.9	1.3	520, 570*sh*	250, 100	This Work
L1	270, 310	34,900, 21,300	390/315	6400	0.9	1.4	530[a]	16[a]	9
L2	270, 340	30,000, 61,400	405/345	4700	0.3	1.7	560[a]	80[a]	9
D1G1	319	102,800	452[a]/310[a]	10,130	0.4[a]	1.0[b]	505[b]	80[b]	19

λ_{abs}: One-photon absorption wavelength in chloroform solutions; ε: Molecular absorption coefficient at λ_{abs}; λ_{em}: emission maximum wavelength in dichloromethane solutions for excitation at λ_{exc}; ϕ: fluorescence quantum yield in dichloromethane solutions determined relative to the *p*-bis-(*o*-methylstyryl)benzene (MSB; $\phi^{ref} = 1$)[20]; τ luminescence lifetime measured in acetonitrile; λ_{TPA}: Maximum two-photon absorption wavelength; σ_{TPA}: Two-photon absorption cross-section, GM for Göppert–Mayer with 1 GM = 10^{-50} cm^4 s photon^{-1} measured from 2×10^{-3} mol L^{-1} solutions of molecules in toluene, via TPEF technique and using a nanosecond OPO pumped by tripled Nd:YAG laser as excitation sources in the 450–650 nm range; the TPA experimental set-up has already been described.[2b,21] *sh*: shoulder.

[a] For facility reasons, different solvents have been used in spectroscopic studies, since no solvatochromic effects were observed in linear absorption (see Supplementary data), in acetonitrile solution.

[b] In chloroform solution.

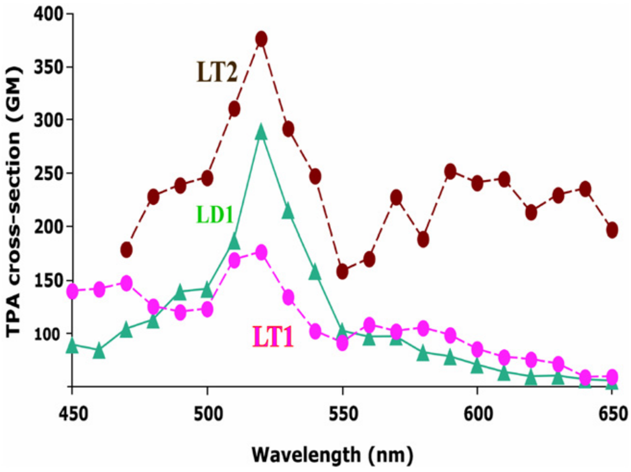


Fig. 4. Two-photon excitation spectra of **LT1**, **LT2** (circles) and **LD1** (triangles) measured in toluene (the experimental uncertainty is ±15%).

the fluorescence lifetime is not modified by the triple bond. The Stokes shift significantly increases from **LT1** to **LT2** (1990 and 3980 cm^{-1}, respectively) and from **LT1** to **LD1** (1990 and 5680 cm^{-1}, respectively). For these compounds, this may be consistent with a greater molecular reorganization between the Franck–Condon excited state and the emitting one as the number of fluorene moieties increases. The increase of the Stokes shift from **LT1** to **L1** (1990 and 6400 cm^{-1}, respectively) confirms the greater rigidity of the alkyne **LT1** with respect to that of **L1**. This rigidity leads to fewer conformational modifications of the excited state of **LT1**. The same trend is observed with bifluorene systems for **LT2** and **L2** (3980 and 4700 cm^{-1}, respectively) in a smaller scale.

The two-photon excitation spectra of **LT1**, **LT2** and **LD1** are reported in Figure 4. All spectra contain three main bands at 460–480, 520 and 560–650 nm (Table 1). **LT2** possesses the highest TPA cross-section of around 350 GM.

In summary, we have synthesized novel 1,10-phenanthroline based chromophores, which have interesting TPA properties (up to 350 GM for **LT2**). These properties, with no significant spectral shift, are strongly enhanced with respect to those of previous ligands[9] (**L1** and **L2**) due to the increase in the electronic delocalization as a result of the introduction of a triple bond. Thus, we can expect higher TPA properties for Ru(II) complexes based on **LT2** than those already observed for the complex involving **L2** ($\leqslant$90 GM[9] in the 700–1000 nm spectral range).

These ligands should lead to several applications in TPA systems, in particular, those based on Ru(II) properties. Studies for (i) optical power limiting applications in the 700–1000 nm spectral range of Ru(II) complexes based on **LT2**[22] and (ii) the synthesis of soluble ligands in biological media are currently in progress.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.01.080.

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18. *Typical experimental procedure and selected data for*: Compound **5a**: Under nitrogen atmosphere, 2-bromo-9,9-dihexylfluorene (4.2 g, 10.1 mmol) was dissolved in 10 mL anhydrous THF. Then, 25 mL $i\mathrm{Pr}_3\mathrm{N}$, 652 mg $\mathrm{Pd(PPh_3)_2Cl_2}$ (1 mmol, 10%), 212 mg CuI (1.1 mmol, 11%) and 2 mL of trimethylsilylacetylene (20 mmol) were added. Reaction mixture was refluxed for 48 h before organic layer was washed twice at room temperature with a 2 M HCl solution, then saturated $\mathrm{NaHCO_3}$ solution and finally with water. After being dried over $\mathrm{Na_2SO_4}$, the solvent was evaporated and the resulting solid solubilized in $\mathrm{Et_2O}$ to eliminate the catalyst by filtration on Celite. The resulting product purified by chromatography on silica eluting with pentane to yield 2 g of a yellow solid (95% yield). mp 69 °C. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 7.69 (m, 1H, $\mathrm{H_3}$); 7.64 (m, 1H, $\mathrm{H_2}$); 7.47 (m, 2H, $\mathrm{H_1}$, $\mathrm{H_7}$); 7.34 (m, 3H, $\mathrm{H_4}$, $\mathrm{H_5}$, $\mathrm{H_6}$); 1.96 (m, 4H, $\mathrm{H_{alkyl}}$); 1.13–1.05 (m, 12H, $\mathrm{H_{alkyl}}$); 0.80 (m, 6H, $\mathrm{H_{alkyl}}$); 0.58 (m, 4H, $\mathrm{H_{alkyl}}$); 0.31 (s, 9H, $\mathrm{H_{TMS}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 151.66; 151.22; 142.31; 141.04; 131.74; 128.14; 127.47; 126.86; 123.47; 121.91; 120.63; 120.06; 106.95; 94.33; 55.75; 41.05; 34.79; 32.17; 30.35; 24.30; 23.23; 22.99; 14.65; 14.58; 0.67. Anal. Calcd for $\mathrm{C_{30}H_{42}Si}$: C, 83.65; H, 9.83. Found: C, 83.76; H, 9.78. IR (KBr): $\nu = 2954\ \mathrm{cm^{-1}}$ ($-\mathrm{C{-}H_{akyl}}$); $\nu = 2856\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2152\ \mathrm{cm^{-1}}$ ($\mathrm{C{\equiv}C}$); $\nu = 1467\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\nu = 1450\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\delta = 760\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aromatic}}$). Compound **5b**: 95% yield. No mp measured. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 7.80–7.75 (m, 3H); 7.68–7.61 (m, 4H); 7.51–7.48 (m, 2H); 7.39–7.33 (m, 4H); 2.05–2.02 (m, 8H, $\mathrm{H_{alkyl}}$); 1.16–1.08 (m, 24H, $\mathrm{H_{alkyl}}$); 0.80–0.68 (m, 20H, $\mathrm{H_{alkyl}}$); 0.32 (s, 9H, $\mathrm{H_{TMS}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 152.44; 152.12; 151.64; 151.54; 141.99; 141.72; 141.36; 141.07; 140.94; 140.17; 134.56; 134.18; 131.84; 129.33; 129.19; 129.05; 127.66; 127.42; 126.91; 126.83; 126.67; 123.56; 122.06;121.79; 120.88; 120.51; 120.37; 120.15; 106.96; 94.54; 55.90; 55.79; 40.98; 32.08; 30.30; 24.39; 23.18; 14.62; 0.72. Anal. Calcd for $\mathrm{C_{55}H_{74}Si}$: C, 86.55; H, 9.77; Si, 3.68. Found: C, 86.28; H, 9.76; Si, 3.45. IR (KBr): $\nu = 2954\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2927\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2856\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2152\ \mathrm{cm^{-1}}$ ($\mathrm{C{\equiv}C}$); $\nu = 1465\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\nu = 1451\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\delta = 740\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aromatic}}$). Compound **6a**: 1.5 g of compound **5a** (3.5 mmol) and $\mathrm{K_2CO_3}$ (482 mg, 3.5 mmol) were dissolved in methanol and ether and the solution was stirred at room temperature for a night. Organic layer was then washed with 20 mL $\mathrm{H_2O}$ and 20 mL brine. After being dried over $\mathrm{Na_2SO_4}$, the solvent was evaporated and the resulting product purified by chromatography on silica eluting with pentane to yield 1.1 g of a yellow oil (88% yield). ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 7.70 (m, 1H, $\mathrm{H_3}$); 7.65 (m, 1H, $\mathrm{H_2}$); 7.49 (m, 2H, $\mathrm{H_1}$, $\mathrm{H_7}$); 7.33 (m, 3H, $\mathrm{H_4}$, $\mathrm{H_5}$,$\mathrm{H_6}$); 3.15 (s, 1H, $\mathrm{H_8}$); 1.95 (m, 4H, $\mathrm{H_{alkyl}}$); 1.14–1.02 (m, 12H, $\mathrm{H_{alkyl}}$); 0.80 (m, 6H, $\mathrm{H_{alkyl}}$); 0.59 (m, 4H, $\mathrm{H_{alkyl}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 151.67; 151.34; 142.55; 140.87; 131.72; 128.25; 127.50; 127.14; 123.53; 120.75; 120.68; 120.17; 85.39; 55.73; 40.94; 32.11; 30.30; 24.30; 23.19; 14.6. Anal. Calcd for $\mathrm{C_{27}H_{37}}$: C, 90.44; H, 9.55. Found: C, 90.44; H, 9.65. IR (KBr): $\nu = 2954\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2105\ \mathrm{cm^{-1}}$ ($\mathrm{C{\equiv}C}$); $\nu = 1450\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\delta = 739\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aromatic}}$); $\delta = 648\ \mathrm{cm^{-1}}$ ($\mathrm{C{\equiv}CH}$). Compound **6b**: (94% yield). No mp determined. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 7.78–7.58 (m, 8H); 7.50–7.47 (m, 2H); 7.32 (m, 3H); 3.13 (s, 1H); 1.97–2.05 (m, 8H, $\mathrm{H_{alkyl}}$); 1.16–1.06 (m, 24H, $\mathrm{H_{alkyl}}$); 0.78–0.71 (m, 20H, $\mathrm{H_{alkyl}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 152.46; 152.13; 151.64; 142.27; 141.84; 141.36; 141.12; 140.90; 140.04; 131.85; 127.68; 127.44; 127.20; 126.89; 126.70; 123.57; 122.08; 120.94; 120.74; 120.53; 120.38; 120.25; 85.43; 55.90; 55.81; 40.98; 40.94; 32.1; 30.31; 30.28; 24.38; 23.19; 14.63. Anal. Calcd for $\mathrm{C_{52}H_{66}}$: C, 90.37; H, 9.62. Found: C, 90.19; H, 9.48. IR (KBr): $\nu = 2953\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2927\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2855\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 1464\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\nu = 1452\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aromatic}}$); $\delta = 740\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aromatic}}$); $\delta = 648\ \mathrm{cm^{-1}}$ ($\mathrm{C{\equiv}CH}$). **LT1**: In a round-bottom flask under inert atmosphere, boronic acid **6a** (2.3 g, 6.4 mmol), tetrakis(triphenylphosphine)palladium(0) (370 mg, 0.32 mmol, 5%) and 5-bromo-1,10-phenanthroline **1** (1.83 g, 7 mmol) were dissolved in pyrrolidine and heated at 70 °C overnight. Then, reaction mixture was dropped in 100 mL of a saturated $\mathrm{NH_4Cl}$ solution and extracted twice with 100 mL $\mathrm{CH_2Cl_2}$. Organic layers were washed with saturated $\mathrm{NH_4Cl}$ (2×50 mL), brine (30 mL) and dried over $\mathrm{Na_2SO_4}$. The brown solid obtained was purified by chromatography on alumina ($\mathrm{CH_2Cl_2}$, 5% $\mathrm{NEt_3}$) before recrystallization from acetonitrile to yield 2.3 g of a beige powder (67% yield). mp: 137 °C. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 9.27 (1H, d, ${}^{3}J = 3.0$ Hz, $\mathrm{H_2}$ or $\mathrm{H_9}$), 9.21 (1H, d, ${}^{3}J = 3.0$ Hz, $\mathrm{H_9}$ or $\mathrm{H_2}$), 8.93 (d, 1H, ${}^{3}J = 8.2$ Hz, $\mathrm{H_4}$ or $\mathrm{H_7}$); 8.26 (d, 1H, ${}^{3}J = 8.2$ Hz, $\mathrm{H_7}$ or $\mathrm{H_4}$); 8.16 (s, 1H, $\mathrm{H_6}$); 7.85–7.64 (m, 6H, $\mathrm{H_3}$, $\mathrm{H_8}$, $\mathrm{H_{11}}$–$\mathrm{H_{13}}$ and $\mathrm{H_{17}}$); 7.39–7.37 (m, 3H, $\mathrm{H_{14}}$–$\mathrm{H_{16}}$); 2.05–2.02 (m, 4H, $\mathrm{H_{alkyl}}$); 1.15–1.08 (m, 12H, $\mathrm{H_{alkyl}}$); 0.79–0.77 (m, 6H, $\mathrm{H_{alkyl}}$); 0.68–0.65 (m, 4H, $\mathrm{H_{alkyl}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 151.65; 151.33; 150.49; 136.38; 131.57; 131.14; 128.43; 127.61; 126.66; 124.12; 124.01; 23.60; 120.78; 120.46; 97.87; 55.87; 41.02; 32.15; 30.33; 24.37; 23.21; 14.62. Anal. Calcd for $\mathrm{C_{39}H_{40}N_2}$, 0.4 $\mathrm{H_2O}$: C, 86.11; N, 5.15. Found: C, 86.17; N, 5.08. $\lambda_{\max}$ (ε) = 368(31,000); 347(34,373); 278(30,780); 242(31,653). IR (KBr): $\nu = 2954\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2856\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\delta = 740\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aro}}$). **LT2**: 42% yield mp: 81 °C. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 9.28 (1H, dd, ${}^{3}J = 4.4$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_2}$ or $\mathrm{H_9}$), 9.22 (1H, dd, ${}^{3}J = 4.2$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_9}$ or $\mathrm{H_2}$), 8.94 (dd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_4}$ or $\mathrm{H_7}$); 8.27 (dd, 1H, ${}^{3}J = 7.94$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_7}$ or $\mathrm{H_4}$); 8.17 (s, 1H, $\mathrm{H_6}$); 7.84–7.63 (m, 12H, $\mathrm{H_3}$, $\mathrm{H_8}$, $\mathrm{H_{11}}$–$\mathrm{H_{17}}$, $\mathrm{H_{21}}$–$\mathrm{H_{23}}$); 7.39–7.29 (m, 3H, $\mathrm{H_{18}}$–$\mathrm{H_{20}}$); 2.12–2.04 (m, 8H, $\mathrm{H_{alkyl}}$); 1.16–1.09 (m, 24H, $\mathrm{H_{alkyl}}$); 0.80–0.75 (m, 20H, $\mathrm{H_{alkyl}}$). ^{13}C NMR (50.32 MHz; 300 K; $\mathrm{CDCl_3}$) 152.48; 152.16; 151.96; 151.63; 151.33; 142.55; 142.01; 141.32; 141.17; 140.84; 139.98; 136.39; 131.63; 131.14; 129.00; 128.82; 127.71; 127.44; 126.97; 126.70; 124.02; 123.57; 122.12; 121.25; 121.04; 120.92; 120.54; 120.39; 100.21; 97.36; 86.59; 64.20; 56.02; 55.81; 53.69; 40.99; 32.12; 32.08; 30.30; 24.40; 23.19; 23.17; 22.95; 14.67; 14.63; 8.80. Anal. Calcd for $\mathrm{C_{64}H_{72}N_2}$, 1.5 $\mathrm{H_2O}$: C, 85.76; N, 3.12; H, 8.58. Found: C, 85.87; N, 3.07; H, 8.43. IR (KBr): $\nu = 2953\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2926\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 2856\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{akyl}}$); $\nu = 1467\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aro}}$); $\nu = 1452\ \mathrm{cm^{-1}}$ ($\mathrm{C{=}C_{aro}}$); $\delta = 741\ \mathrm{cm^{-1}}$ ($\mathrm{C{-}H_{aro}}$). **LD1**: Compound **7**[19] (1 g, 0.89 mmol), 5-bromo-1,10-phenanthroline (219 mg, 0.85 mmol) and tetrakis(triphenylphosphine)-palladium(0) (31 mg, 0.026 mmol, 3%) were dissolved under inert atmosphere in 10 mL toluene and 9 mL of a 1 M sodium carbonate solution. Reaction mixture was refluxed under vigourous stirring for 48 h. Organic layer was then extracted with pentane, washed with water and dried over $\mathrm{Na_2SO_4}$. The 1.4 g of the yellow solid obtained after evaporation of the solvent was purified by chromatography on alumina ($\mathrm{CH_2Cl_2}$, 1% $\mathrm{NEt_3}$) before solubilizing in 10 mL $\mathrm{CH_2Cl_2}$ and washed with water. Evaporation to dryness of the organic solution yielded 0.58 g of a white powder (52% yield). No mp measured. ^{1}H NMR (499.84 Hz; 300 K; $\mathrm{CDCl_3}$) 9.28 (1H, dd, ${}^{3}J = 4.4$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_2}$ or $\mathrm{H_9}$), 9.22 (1H, dd, ${}^{3}J = 4.2$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_9}$ or $\mathrm{H_2}$), 8.94 (dd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{5}J = 1.6$ Hz, $\mathrm{H_4}$ or $\mathrm{H_7}$); 8.27 (dd, 1H, ${}^{3}J = 7.94$ Hz,

$^5J = 1.6$ Hz H_7 or H_4); 8.17 (s, 1H, H_6); 7.84–7.63 (m, 19H, H_3, H_8, H_{11}–H_{16}, H_{20}–H_{24}, H_{28}–H_{33}); 7.39–7.29 (m, 6H, H_{17}–H_{19}, H_{25}–H_{27}); 2.14–2.05 (m, 12H_{alkyl}); 5.30 (s, 4H, $H_{CH_2Cl_2}$); 1.27–1.09 (m, 36 H_{alkyl}); 0.87–0.70 (m, 30 H_{alkyl}). ^{13}C NMR (50.32 MHz; 300 K; $CDCl_3$) 152.49; 152.25; 152.08; 151.62; 150.89; 150.73; 147.22; 146.45; 143.69; 143.43; 141.44; 141.38; 141.33; 141.28; 140.71; 140.03; 138.24; 136.57; 135.22; 129.51; 128.81; 127.78; 127.47; 127.18; 127.06; 126.92; 125.95; 125.81; 125.27; 124.03; 123.59; 123.39; 122.54; 122.41; 120.93; 120.63; 120.44; 56.15; 55.89; 41.09; 32.13; 30.37; 30.32; 24.59; 24.44; 23.20; 14.65; 14.63. Anal. Calcd for $C_{99}H_{108}N_2$, $2CH_2Cl_2$, 1 H_2O: C, 79.47; N, 1.91. Found: C, 79.52; N, 1.83.

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