



Highly fluorescent intramolecular *dimmers* of two pyrenyl-substituted fluorenes bridged by 1,6-hexanyl: synthesis, spectroscopic, and self-organized properties

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ABSTRACT

Two intramolecular *dimmers* of 4-, 8-pyrenyl-substituted fluorenes bridged by 1,6-hexanyl unit have been synthesized. They showed very strong fluorescent emission with the emission peak at around 450 nm and fluorescence efficiency as high as ~0.9. The absorption spectra also had high extinction coefficients. The cyclic voltammetric curves showed that they can be used as electron-donating materials. The DSC results suggested the *dimmers* have higher glass transition temperature. It was also found that these novel *dimmers* can self-organize into spherical particles from the solutions due to evaporation of the solvent.

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Fluorene and its analogs have shown many attractive properties, such as wide energy gap, high luminescent efficiency, tunable emission color and easy functionalization at the 9-position of the fluorene ring, which have received considerable attentions for applications in the fields of optoelectronic devices.¹ In comparison with fluorene-based macromolecules, the fluorene derivatives of low molecular weight have advantages in easily controlling the structure, purification and pure emission color.² However, the small molecule derivatives tend to crystallize because of the heat effect leading to deteriorated film quality. The solutions to this problem have been reported based on introducing bulky aromatic groups or spiro structures to the molecules, which complicated the synthesis process.³

In this Letter, we report on a simple and effective way to prepare amorphous fluorene derivatives, by using a novel intramolecular *dimmer* structure.⁴ Hexanyl was used as a linker to bridge the two fluorene moieties in order to modulate the solubility of the compounds and the distance between the chromophores. The fluorene rings were also be functionalized by introducing pyrenyl units at the 2- and 7-positions to improve the extinction coefficient, fluorescence quantum yield and thermal stability.⁵ In addition, we added carbazolyl units into the *dimmer* molecule to demonstrate the flexibility of tuning the electronic properties by introducing electron-donating/accepting units to the molecule.⁶ It

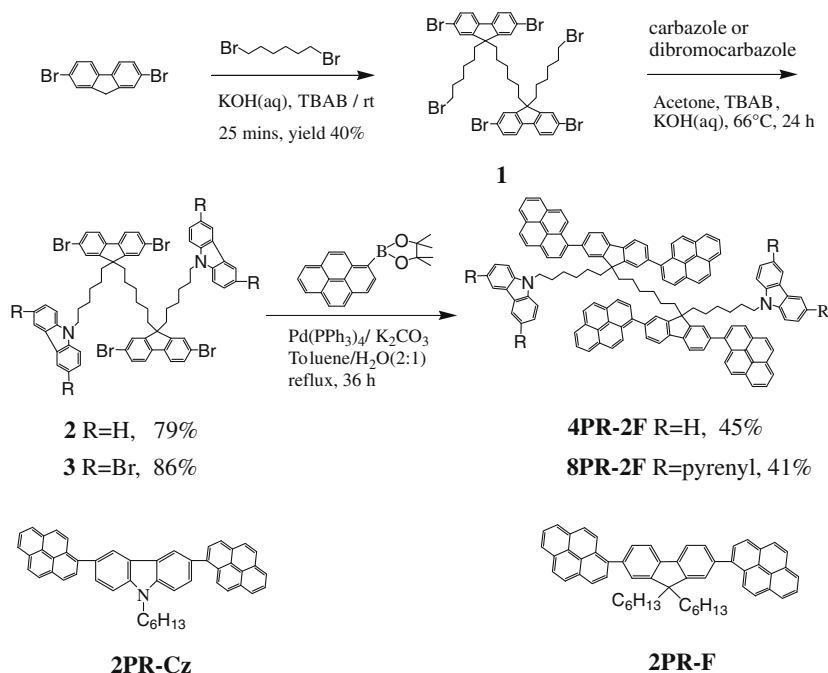
has been found that the *dimmer* compounds, **4PR-2F** and **8PR-2F** have higher extinction coefficient, higher glass transition temperature and lower band gap in contrast to their counterparts **2PR-F** and **2PR-Cz**.

Scheme 1 outlines the synthetic routes for the two *dimmers*, **4PR-2F** and **8PR-2F**. Detailed synthesis process is described in References and notes. Compound **1** was easily obtained by the reaction between 2,7-dibromofluorene (DBF) and 1,6-dibromohexane (DBH) with the optimized ratio (2:3, mol/mol), which led to a moderate yield (40%). The reaction between **1** and carbazole was conducted in acetone and KOH aq 50% mixture using tetrabutylammonium bromide (TBAB) as the phase transfer catalyst to provide compound **2** with a yield of 79%. The parallel reaction of **1** with 3,6-dibromocarbazole-yielded compound **3** (yield 86%). 1-Bromopyrene, synthesized according to the literature⁷ was subjected to halogen–lithium exchange and subsequent reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give pyrene boronic acid ester (PyBOH, yield 86%). Suzuki cross-coupling between **2** and PyBOH resulted in **4PR-2F** (yield, 45%). In a similar way, **8PR-2F** was synthesized with a yield of 41% from **3** and PyBOH.⁸ The compounds **2PR-Cz** and **2PR-F** were also synthesized by a Suzuki coupling reaction in the yield of 63% and 72%, respectively.

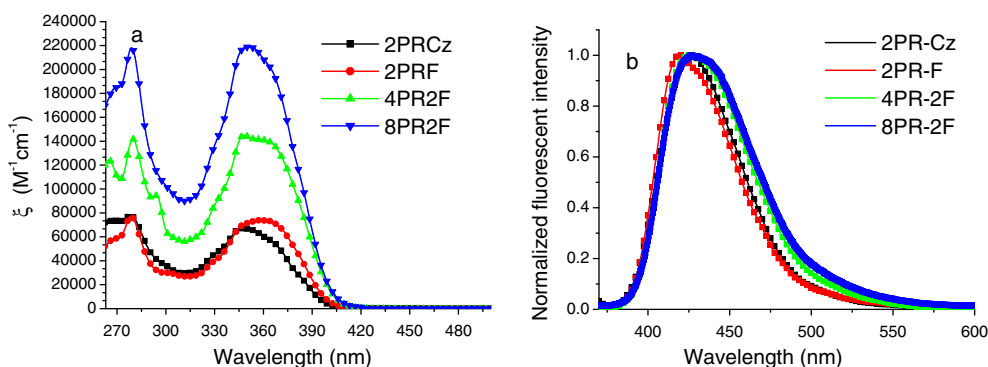
The absorption and emission spectra of **2PR-Cz**, **2PR-F**, **4PR-2F**, and **8PR-2F** in dilute THF solution are shown in Figure 1. The optical absorption and emission results are summarized in Table 1. It is noted that the molar extinction coefficient increases significantly by introducing more pyrenyl units into the molecule. It is almost doubled from **2PR-F** (log ϵ = 4.88) to **4PR-2F** (log ϵ = 5.16). And

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Scheme 1. Structure and synthetic routes for 4PR-2F and 8PR-2F.

Figure 1. UV-vis absorption (a) and emission (b) spectra of 2PR-Cz, 2PR-F, 4PR-2F, and 8PR-2F in THF (concentration, 10^{-7} – 10^{-6} M).Table 1
Spectroscopic and electrochemical properties of 2PR-Cz, 2PR-F, 4PR-2F, and 8PR-2F

	Abs ^a , λ_{max} (nm)		PL ^a , λ_{max} (nm)		HOMO ^b (eV)	LUMO ^b (eV)	ΔE^b (eV)	ϕ^c	Log ϵ_{max}^d
	Solution	Film	Solution	Film					
2PR-Cz	349	368	426	442	-5.81	-2.66	3.15	0.85	4.81
2PR-F	359	368	419	458	-5.93	-2.74	3.19	1.00	4.88
4PR-2F	349	368	426 Broad	449	-5.62	-2.64	2.98	0.86	5.16
8PR-2F	349	358	426 Broad	455	-5.60	-2.56	3.04	0.91	5.36

^a The excitation light wavelength was at 360 nm, and the film was prepared by spin-coated from its THF solution on quartz plate.

^b The HOMO energy level and LUMO energy level were estimated according to the literature, ΔE (band gap) = HOMO – LUMO.⁹

^c The fluorescence quantum yields of the above compounds in THF solution were measured using a dilute solution of 9,10-diphenylanthracene ($\phi \sim 0.9$) in cyclohexane as the standard.¹⁰

^d The molar absorption coefficient was measured at the absorption maxima (λ_{max}).

there is about 66% increase from 4PR-2F (log ϵ = 5.16) to 8PR-2F (log ϵ = 5.36), which is critical for photo responsive devices.

The emission spectra of *dimmers* are a little broader than that of 2PR-F and 2PR-Cz, which might be attributed to the superimposition of the increased emitting units with different conjugated length. Additionally, the emission maxima from 2PR-Cz to 8PR-2F almost keep constant. All these compounds exhibit respectable quantum efficient yields in THF as given in Table 1.

Unlike 2PR-F and 2PR-Cz, the *dimmer* materials tend to form homogenous films via spin-coating procedure. Figure 2 shows the absorption and emission spectra of the spin-coated films. The absorption maxima of 2PR-Cz, 2PR-F, and 4PR-2F are all red-shift to 368 nm with a long tail (475–550 nm) relative to their solution counterparts. Interestingly, 8PR-2F shows less red-shift and a narrower absorption peak without the long tail absorption. This could be attributed to the large steric hindrance arising from the four

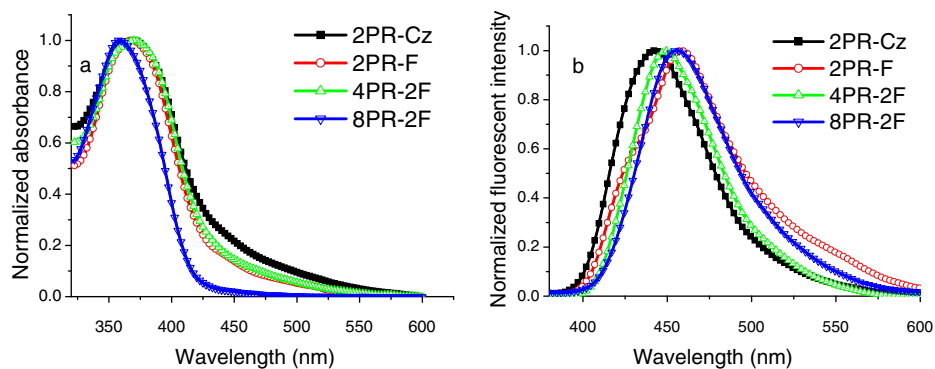


Figure 2. UV-vis absorption (a) and emission (b) spectra of **2PR-Cz**, **2PR-F**, **4PR-2F**, and **8PR-2F** films.

large chromospheres. The emission peak of **2PR-F** red-shift about 39 nm with the broadest emission profile among the four compounds compared with its solution counterpart. Compounds **4PR-2F** and **8PR-2F** red-shift only 23 nm and 29 nm, suggesting the *dimmer* structure could be beneficial for preventing severe aggregation in film state, especially for **4PR-2F**, in which the broad emission tail is not observed.

The cyclic voltammetric curves of **2PR-Cz**, **2PR-F**, **4PR-2F**, and **8PR-2F** are shown in Figure 3. All compounds exhibit quasi-reversible oxidative and reductive cycles. The oxidation onset potentials of **4PR-2F** and **8PR-2F** are lower compared with that of **2PR-Cz** and **2PR-F**, which suggests that **4PR-2F** and **8PR-2F** could be used as strong electron-donating materials. It is also revealed that the de-doping process of oxidation cycle show a broad peak possibly arising from a multiple-electron involved process. The corresponding data is also summarized in Table 1.

DSC measurements were performed to understand the thermal properties. Glass transition temperatures (T_g) were measured to be 81.2, 114.6, 126.7 and 164.7 °C for **2PR-F**, **2PR-Cz**, **4PR-2F**, and **8PR-2F**, respectively. The elevation of T_g from **2PR-F** to **8PR-2F** is consistent with the increased ratio of rigid aromatic units to alkyl chains. Compound **8PR-2F** has four more pyrenyl units in the molecule and it shows higher T_g compared with **4PR-2F**. Since materials with higher T_g tend to show stronger capacity to resist self-crystallization under unfavorable heating condition, the *dimers* could be more suitable for making optically stable thin-film devices, such as organic light emitting diodes (OLED) and laser devices.

In order to understand the molecular structure of **4PR-2F** and **8PR-2F**, quantum chemistry calculations were performed. Two optimized conformations were obtained in a so-called *open* and *close* state (Fig. 4) named according to the distance of the two

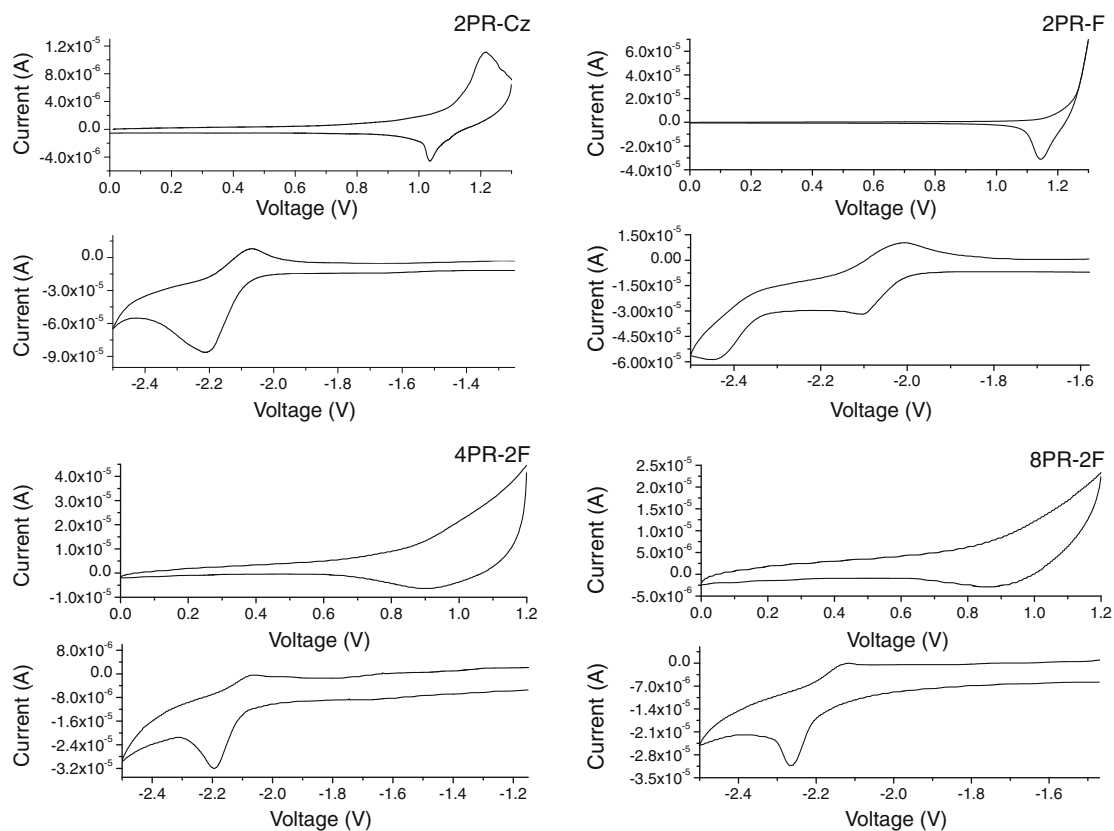


Figure 3. The CV curves of **2PR-Cz**, **2PR-F**, **4PR-2F**, and **8PR-2F** on glassy carbon substrates at a sweep rate of 100 mV s⁻¹.¹¹

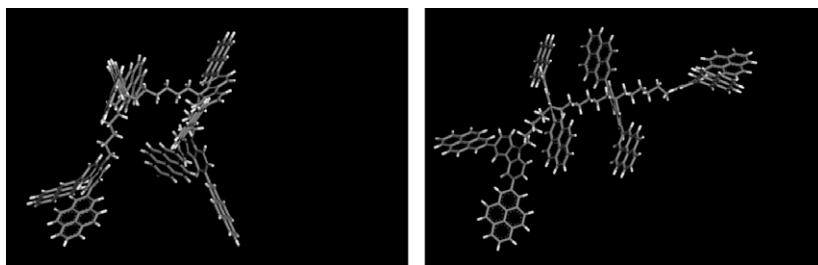


Figure 4. Optimized structures of **8PR-2F**.

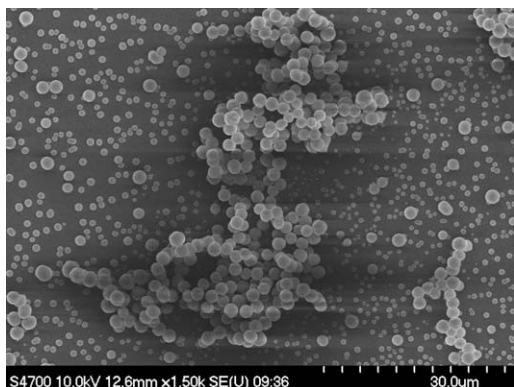


Figure 5. SEM image of drop-casted **8PR-2F** particles.

carbazole-contained chromospheres arising from the free moving of three alkyl chains. Both conformations exhibit a highly steric three-dimensional (3D) structure, which is responsible for the isotropic electronic properties of the devices during a solution-based process. The 3D and rigid structure could assist in reducing the intermolecular interaction in the solid state, as proved by their spectroscopic data.

Inspired by their 3D structure, the self-organization behavior of the *dimmers* was studied. When the solvent evaporated naturally from the **4PR-2F** and **8PR-2F** solutions at room temperature, solid powders with perfect sphere morphology (Fig. 5) were precipitated from the solutions. And the size of the amorphous spheres was tunable to some extent by a simple changing of the concentration. However, no such spherical morphology was formed from **2PR-Cz** or **2PR-F** solutions under the same condition. The detailed formation mechanism of the morphology structure is warrant to be investigated.

In summary, new intermolecular fluorene *dimmers* have 4- and 8-substituted pyrenyls in the fluorene rings have been synthesized. These fluorene *dimmers* tend to form amorphous structure arising from the high steric hindrances of the 3D molecular structure. DSC results suggested the *dimmers* could be more suitable for making stable films for organic electronic devices. Optical properties revealed that the *dimmers* have higher molar extinction coefficients and can prevent severe aggregation in film state. The cyclic voltammetric curves showed that the *dimmers* could be used as strong electron-donating materials. And also the SEM data exhibited an interesting self-organization behavior that deserved for further study.

Acknowledgments

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2009BAK64B00-03), Chinese Academy of Sciences (Grant No. KGCX2-YW-118), "Bairen program" of CAS, and Shanghai Science and Technology Committee (Grant No. 08JC1421900) for financial supports.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.136.

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- Compound **4PR-2F**: A mixture of **2** (0.32 g, 0.26 mmol), 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (0.42 g, 1.3 mmol), potassium carbonate (0.71 g, 5.2 mmol), and Pd(PPh₃)₄ (60 mg, 0.05 mmol) in 15 mL of toluene/H₂O (2:1, v/v) was degassed for 30 min and then heated to reflux for 36 h. The mixture was extracted with CHCl₃ and the organic layer was washed with water and brine, and then dried over anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography on silica gel, and then recrystallized in CH₂Cl₂/ethanol to get slightly green solid (0.2 g, yield 45%). Mp 251.7–252.7 °C; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.13 (m, 12H), 8.06–7.92 (m, 24H), 7.87 (d, 4H, J = 9 Hz), 7.80 (d, 4H, J = 7.5 Hz), 7.54 (m, 8H), 7.30 (t, 4H, J = 7.5 Hz), 7.23 (d, 4H, J = 8 Hz), 7.12 (t, 4H, J = 7.5 Hz), 4.09 (t, 4H, J = 7 Hz), 1.97 (m, 8H), 1.66 (m, 4H), 1.17 (m, 4H), 1.11 (s, 8H), 0.88 (s, 8H); ¹³C NMR (500 MHz, CDCl₃, ppm) δ 150.876, 140.285, 139.972, 139.921, 138.107, 131.465, 130.885, 130.482, 129.512, 127.600, 127.392, 127.343, 125.948, 125.472, 125.224, 125.067, 125.035, 124.902, 124.763, 124.614, 122.711, 120.230, 118.601, 108.516, 55.244, 42.802, 40.326, 40.080, 29.836, 29.754, 28.733, 26.860, 24.101, 23.959; MALDI-TOF MS: m/z 1713.7. Anal. Calcd for C₁₃₂H₁₀₀N₂: C, 92.49; H, 5.88; N, 1.63. Found: C, 92.15; H, 5.60; N, 1.60. Compound **8PR-2F**: A flask charged with **3** (0.32 g, 0.2 mmol), 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (0.6 g, 1.86 mmol), potassium carbonate (1.2 g, 8.7 mmol), Pd(PPh₃)₄ (57 mg, 0.05 mmol), and 21 mL of toluene/H₂O (2:1, v/v) was degassed for 30 min. The solution was heated to reflux for 36 h, and then poured into 50 mL H₂O and extracted with CHCl₃. The

organic layer was washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on silica gel, and recrystallized in $CHCl_3$ /ethanol to get slightly green solid (0.21 g, yield 41%). Mp 278.1–279.0 °C; 1H NMR (500 M, $CDCl_3$, ppm) δ 8.25 (s, 4H), 8.17–7.90 (m, 60H), 7.80 (m, 12H), 7.74 (d, 4H, $J = 7.5$ Hz), 7.55 (dd, 4H, $J = 1$ Hz, 1 Hz), 7.54 (s, 4H), 7.47 (d, 4H, $J = 7.5$ Hz), 7.39 (d, 4H, $J = 8.5$ Hz), 4.22 (t, 4H, $J = 7$ Hz), 1.93 (m, 8H), 1.81 (m, 4H), 1.26 (m, 4H), 1.15 (m, 4H), 1.05 (s, 4H), 0.90 (m, 4H), 0.84 (m, 4H); ^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 150.851, 140.107, 139.972, 139.889, 138.517, 138.012, 131.929, 131.475, 131.381, 130.979, 130.793, 130.413, 130.155, 129.516, 128.722, 128.639, 128.458, 128.130, 127.537, 127.425, 127.311, 127.254, 127.182, 125.901, 125.822, 125.577, 125.184, 125.158, 125.023, 124.972, 124.957, 124.927, 124.812, 124.700, 124.560, 124.531, 122.958, 122.335, 119.748,

108.539, 55.208, 43.138, 40.279, 40.271, 39.936, 29.790, 29.582, 28.790, 26.778, 24.064, 23.830; MALDI-TOF MS: m/z 2514.8. Anal. Calcd for $C_{196}H_{132}N_2$: C, 93.60; H, 5.29; N, 1.11. Found: C, 93.45; H, 5.62; N, 1.02.

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11. The electrochemical behavior of **2PR-Cz**, **2PR-F**, **4PR-2F**, and **8PR-2F** was investigated by cyclic voltammetry (CV) with a standard three electrodes (a glassy carbon-working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode) electrochemical cell in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile solution under nitrogen with a scanning rate of 100 mV/s at room temperature.