Electronic Supplementary Information

Superacid-Catalyzed Friedel–Crafts Polyhydroxyalkylation: A Straightforward Method to Construct Sky-Blue Thermally Activated

Delayed Fluorescence Polymers

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Experimental

General Information

All reagents and solvents were purchased from commercial sources. In addition, tetrahydrofuran and toluene were dried by sodium-potassium alloy. ¹H NMR and ¹³C NMR spectra were recorded by Bruker Advanced II (400 MHz) spectrometers using CDCl₃ as solvent and tetramethyl silane as the internal standards. High resolution mass spectra (HRMS) were recorded using a Thermo Scientific LTQ Orbitrap XL mass spectrometer with an electrospray ionization (ESI) source. Gel permeation chromatography (GPC) was carried out on a Waters 2690 D Separations Module using Water 2410 Refractive Index Detector, Polystyrene Standard and THF as the solvent. UV-vis absorption spectra were performed on a Shimadzu UV-2700 spectrophotometer. PL spectra were collected on a Hitachi F-4600 fluorescence spectrophotometer. The transient photoluminescence decay curves were measured by a single photo counting spectrometer from Edinburgh Instruments (FLS920). Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics) and all the samples were excited at their maximum absorption wavelength. The optimal molecular geometry was calculated using the DFT with Gaussian 09. Ground state geometry optimization was performed using the B3LYP exchange-correlation functional, the def2-SVP basis set and the density functional dispersion correction with Becke-Johnson damping [DFT-D3(BJ)].



Scheme S1. Synthetic route of DMAC-DPS-F and DMAC-DPS-Cz.

monomer synthesis

1-bromo-4-((4-fluorophenyl)sulfonyl)benzene, 9-hexyl-9H-carbazole (M2) and 1methylindoline-2,3-dione (M3) were synthesized according to the literature methods.¹⁻³ 10-(4-((4-fluorophenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-DPS-F). In twin-neck round bottom flask. 1-bromo-4-((4а fluorophenyl)sulfonyl)benzene (930 mg, 3 mmol), 9,9-dimethyl-9,10-dihydroacridine (627 mg, 3 mmol), palladium acetate (30 mg, 0.13 mmol), tri-tert-butylphosphonium tetrafluoroborate (120 mg, 0.41 mmol) and sodium tert-butoxide (780 mg, 8 mmol) were dissolved in dry toluene (30 mL) under argon atmosphere. After stirring at 110 °C for 2 days, the reaction mixture was poured into water (300 mL) and extracted with 100 mL CH₂Cl₂ for three times. Then the combined organic phases were dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/CH₂Cl₂ v/v 2:3) to give white powder (1.1 g, 80 %). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.14 \text{ (d, } J = 8.6 \text{ Hz}, 2\text{H}), 8.11-8.04 \text{ (m, 2H)}, 7.50 \text{ (d, } J = 8.6 \text{ Hz}, 2\text{H})$ 2H), 7.48-7.42 (m, 2H), 7.26 (dd, J = 9.4, 7.7 Hz, 3H), 7.05-6.92 (m, 4H), 6.31-6.17 (m, 2H), 1.65 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 166.94, 164.39, 162.53, 146.58, 140.25, 140.15, 137.33, 137.30, 131.59, 130.86, 130.78, 130.69, 130.24, 126.41, 125.38, 121.67, 116.97, 116.74, 114.92, 36.17, 30.76. HRMS (ESI) m/z calcd for $C_{27}H_{23}FNO_2S^+$ (M+H)⁺ 444.14280, found 444.14255.

10-(4-((4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)sulfonyl)phenyl)-9,9-dimethyl-

9,10-dihydroacridine (DMAC-DPS-Cz). In a twin-neck round bottom flask, sodium hydride (60%, 120 mg, 3 mmol) was added to a solution of 3,6-di-tert-butyl-9Hcarbazole (420 mg, 1.5 mmol) in dry THF (5 mL) under argon condition. After stirring at 50 °C for 2 h, DMAC-DPS-F (444 mg, 1 mmol) in dry THF (5 mL) was added and then the mixture was stirred at 65 °C for 24 h. After cooling, the reaction mixture was poured into water (300 mL) and extracted with 100 mL CH₂Cl₂ for three times. Then the combined organic phases were dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/CH₂Cl₂ v/v 2:3) to give white powder (422 mg, 60 %). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 8.3 Hz, 4H), 8.13 (d, J = 0.9 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.52-7.42 (m, 6H), 7.07-6.93 (m, 4H), 6.37-6.28 (m, 2H), 1.67 (s, 6H), 1.46 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 144.15, 143.33, 140.24, 138.46, 138.22, 131.74, 130.84, 130.47, 129.76, 126.53, 126.47, 125.41, 124.12, 124.05, 121.75, 116.56, 115.08, 109.19, 36.24, 34.82, 31.96, 30.76. HRMS (ESI) m/z calcd for C₄₇H₄₇N₂O₂S⁺ (M+H)⁺ 703.33528, found 703.33502.



Figure S1. TGA traces of TADF polymers PACDPS recorded at a heating rate of 10 °C min⁻¹.



Figure S2. Fluorescence spectra (black line) and phosphorescence spectra (red line) of (a) DMAC-DPS-Cz and (b) PACDPS-0 in the neat film.



Figure S3. Fluorescence spectra (black line) and phosphorescence spectra (red line) of (a) PACDPS-5, (b) PACDPS-10 and (c) PACDPS-15 in the neat films.



Figure S4. Temperature dependence of the transient PL decay spectra in 10 wt% mCP doped films for (a) PACDPS-5, (b) PACDPS-10 and (c) PACDPS-15.



Figure S5. ¹H NMR spectrum of PACDPS-0 in CDCl₃ (400 MHz).



Figure S6. ¹³C NMR spectrum of PACDPS-0 in CDCl₃ (100 MHz).



Figure S7. ¹H NMR spectrum of PACDPS-5 in CDCl₃ (400 MHz).



Figure S8. ¹³C NMR spectrum of PACDPS-5 in CDCl₃ (100 MHz).



Figure S9. ¹H NMR spectrum of PACDPS-10 in CDCl₃ (400 MHz).



Figure S10. ¹³C NMR spectrum of PACDPS-10 in CDCl₃ (100 MHz).



Figure S11. ¹H NMR spectrum of PACDPS-15 in CDCl₃ (400 MHz).



Figure S12. ¹³C NMR spectrum of PACDPS-15 in CDCl₃ (100 MHz).

	$S_1/T_1/\Delta E_{\rm ST} \ [{ m eV}]^{ m a}$	$S_1/T_1/\Delta E_{\rm ST} \ [{ m eV}]^{ m b)}$	HOMO/LUMO [eV] ^{a)}
DMAC-DPS-Cz	3.20/2.84/0.36	2.94/2.77/0.17	-4.89/-1.57
PACDPS-15	3.05/3.03/0.02	2.99/2.75/0.24	-4.79/-1.50

Table S1. The calculated and experimental data of DMAC-DPS-Cz and PACDPS-15.

^{a)}Theoretical data by DFT theory calculations at B3LYP-D3(BJ)/def2-SVP level; ^{b)}Experimental data calculated from the onset of the fluorescence and phosphorescence spectra in the neat film.

References

- J. Zhao, Y. Yu, X. Yang, X. Yan, H. Zhang, X. Xu, G. Zhou, Z. Wu, Y. Ren and W.-Y. Wong, ACS Appl. Mater. Interfaces, 2015, 7, 24703-24714.
- J. Huang, Z. Xu, Z. Cai, J. Guo, J. Guo, P. Shen, Z. Wang, Z. Zhao, D. Ma and B. Z. Tang, J. Mater. Chem. C, 2019, 7, 330-339.
- A. Singh, D. Zhang, C. C. Tam, L. W. Cheng, K. M. Land and V. Kumar, J. Organomet. Chem., 2019, 896, 1-4.