

Supplementary Materials for

Molecular defect-containing bilayer graphene exhibiting brightened luminescence

Xin-Jing Zhao, Hao Hou, Peng-Peng Ding, Ze-Ying Deng, Yang-Yang Ju, Shun-He Liu,
Yu-Min Liu, Chun Tang, Liu-Bin Feng, Yuan-Zhi Tan*

*Corresponding author. Email: yuanzhi_tan@xmu.edu.cn

Published 28 February 2020, *Sci. Adv.* **6**, eaay8541 (2020)
DOI: 10.1126/sciadv.aay8541

This PDF file includes:

- Fig. S1. ^1H NMR spectrum of polyphenylene precursor.
- Fig. S2. ^{13}C NMR spectrum of polyphenylene precursor.
- Fig. S3. Bent structure of **1**.
- Fig. S4. ^1H NMR spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$.
- Fig. S5. ^{13}C NMR spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4/\text{CS}_2$.
- Fig. S6. ^1H - ^1H COSY spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$.
- Fig. S7. ^{13}C - ^1H COSY spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$.
- Fig. S8. $\text{H}\cdots\text{H}$ proximity in **1**.
- Fig. S9. ^1H NMR spectra of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$ at different concentrations.
- Fig. S10. ^1H NMR spectra of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$ at different temperatures.
- Fig. S11. Structure of **1** (left) and **2** (right).
- Fig. S12. Time-resolved fluorescence spectrum of **1**.
- Table S1. Ultraviolet-visible absorption parameters of **1** and **2**.

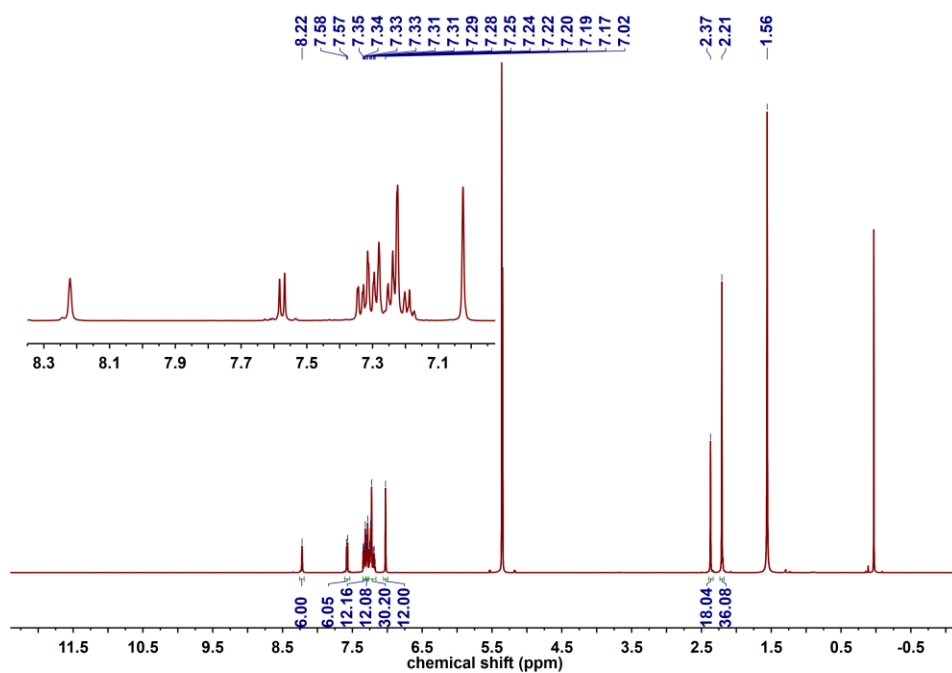


Fig. S1. ^1H NMR spectrum of polyphenylene precursor. (600 MHz, CD_2Cl_2): $\delta =$ 8.22 (s, 6H), 7.58 (d, 6H), 7.35-7.31 (m, 12H), 7.29-7.28 (m, 12H), 7.25-7.17 (m, 30H), 7.02 (s, 12H), 2.37 (s, 18H), 2.21 (s, 36H) ppm.

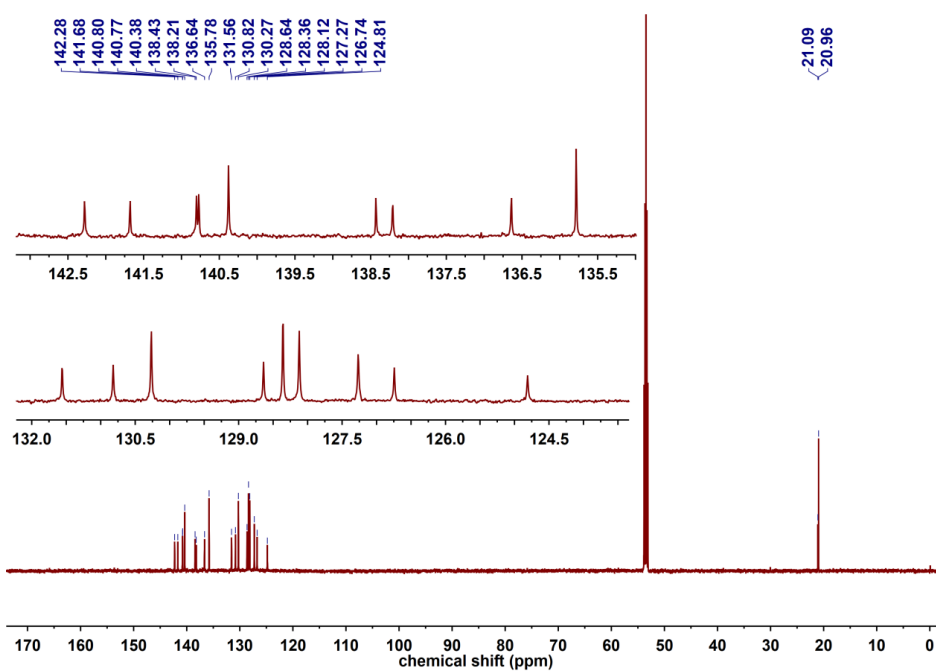


Fig. S2. ^{13}C NMR spectrum of polyphenylene precursor. (150 MHz, $\text{CD}_2\text{Cl}_2/\text{CS}_2$): $\delta =$ 142.28, 141.68, 140.80, 140.77, 140.38, 138.43, 138.21, 136.64, 135.78, 131.56, 130.82, 130.27, 128.64, 128.36, 128.12, 127.27, 126.74, 124.81, 21.09, 20.96 ppm.

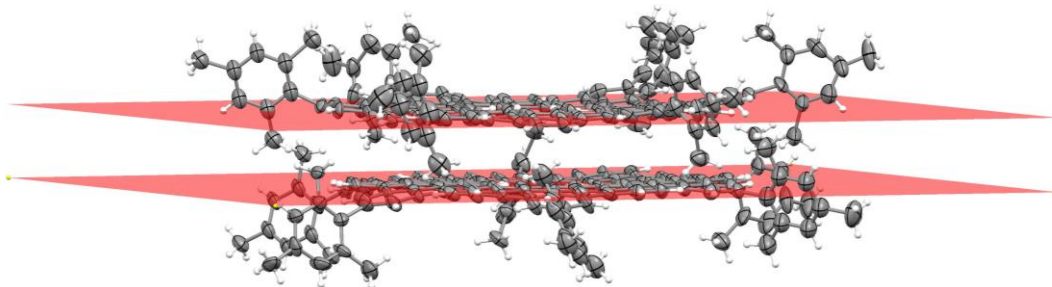


Fig. S3. Bent structure of 1. As shown the mesityl groups were bent outward the planar of inner aromatic core (shown in red) by a mean distance of 2.0 Å.

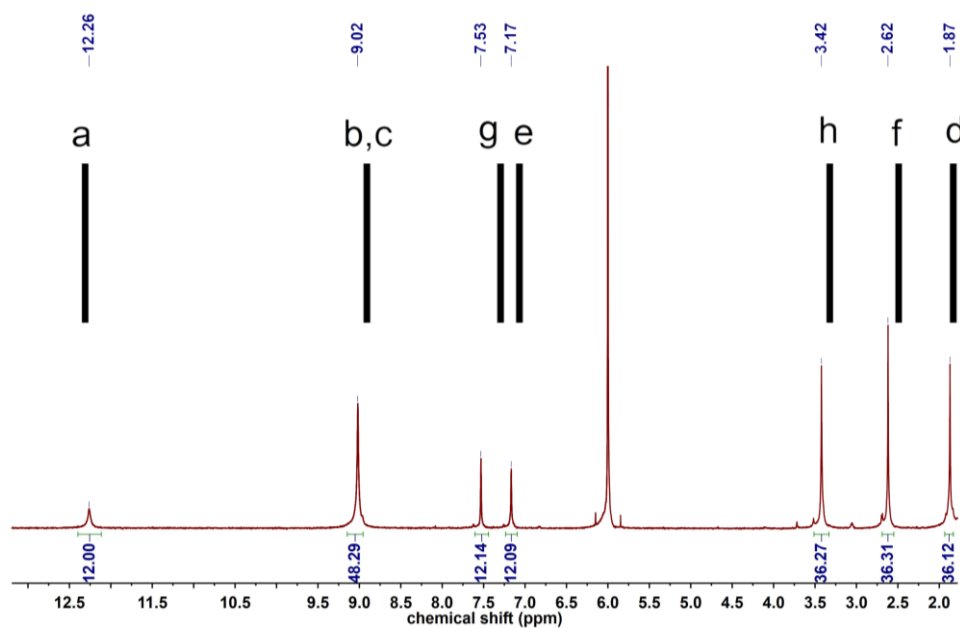


Fig. S4. ^1H NMR spectrum of 1 in $\text{C}_2\text{D}_2\text{Cl}_4$. ^1H NMR of compound **1**. (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): $\delta = 12.26$ (s, 12H), 9.02 (s, 48H), 7.53 (s, 12H), 7.17 (s, 12H), 3.42 (s, 36H), 2.62 (s, 36H), 1.87 (s, 36H) ppm. The theoretic NMR spectrum of **1** was calculated using the GAUSSIAN 16 program package, represented as black lines. The B3LYP functional and the 6-31G* basis sets were employed. The calculated ^1H NMR spectrum of **1** is in good agreement with the experimental patterns.

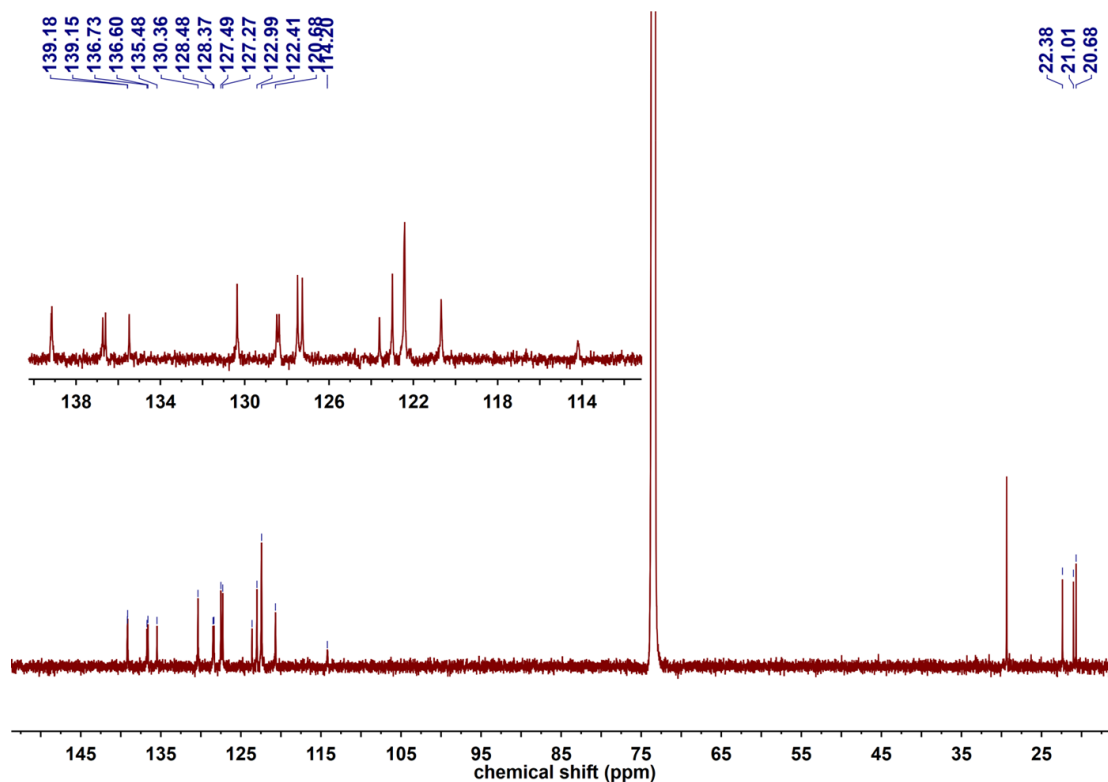


Fig. S5. ^{13}C NMR spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4/\text{CS}_2$. (150 MHz, $\text{C}_2\text{D}_2\text{Cl}_4/\text{CS}_2$): $\delta =$ 139.18, 139.15, 136.73, 136.60, 135.48, 130.36, 128.48, 128.37, 127.49, 127.27, 123.61, 122.99, 122.41, 120.68, 114.20, 22.38, 21.01, 20.68 ppm. We could see each methyl of mesityl group is chemically inequivalent, which clearly demonstrates the bilayer structure of **1**. The peaks at 29.5 ppm is assigned to the signal of hexane. According to asymmetric unit of **1**, there should be 17 peaks in the aromatic range, however, only 15 peaks were observed, due to the overlap of signals.

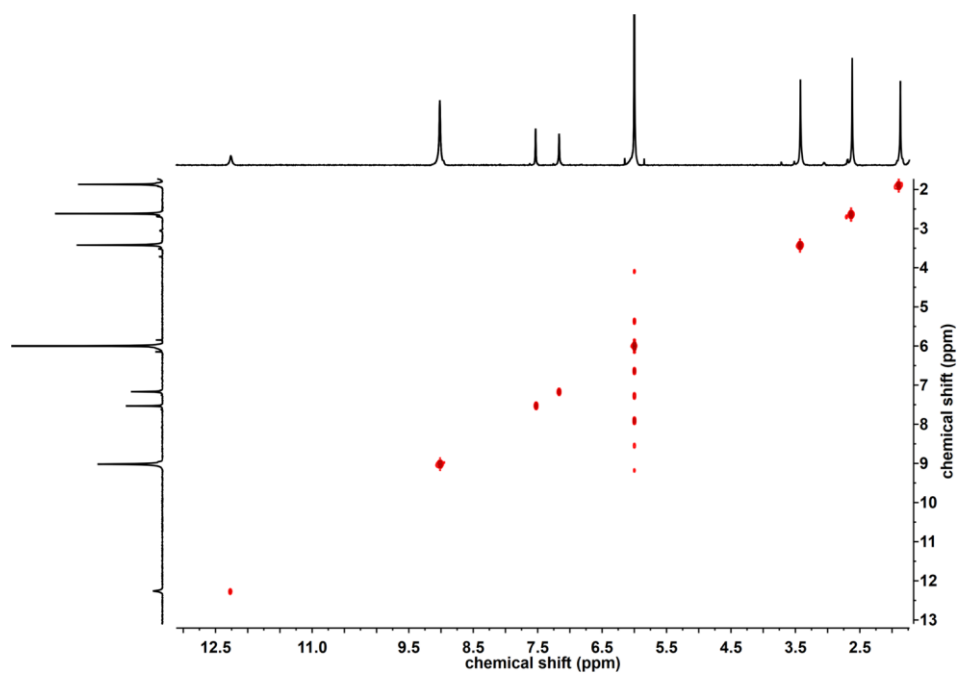


Fig. S6. ^1H - ^1H COSY spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$.

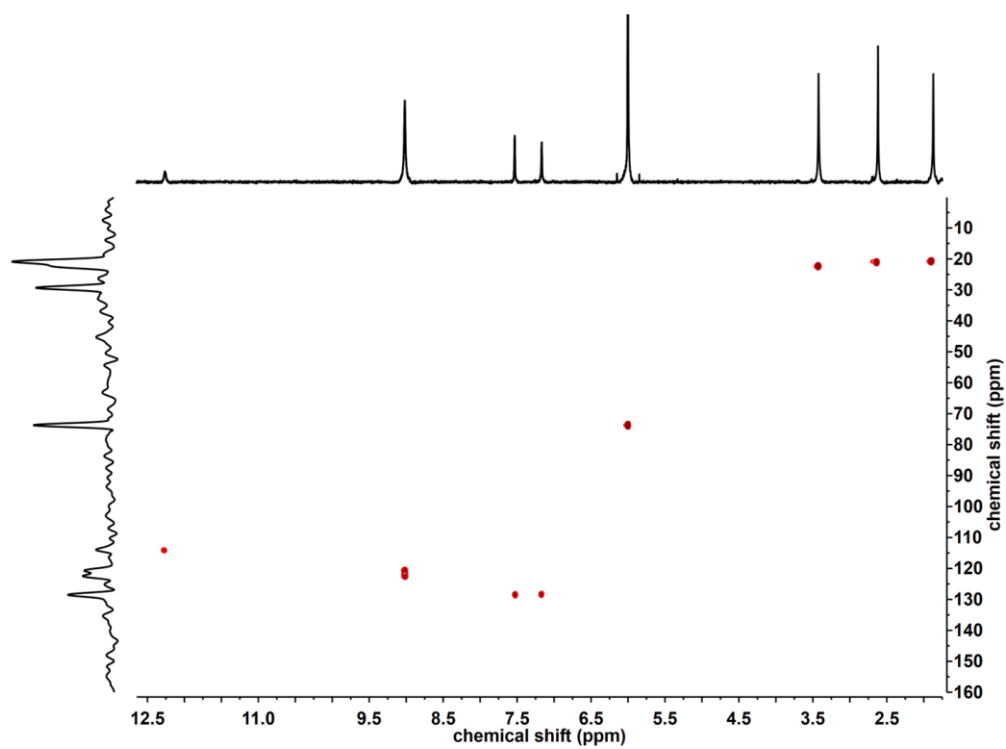


Fig. S7. ^{13}C - ^1H COSY spectrum of **1** in $\text{C}_2\text{D}_2\text{Cl}_4$. As shown, three methyl groups of mesityl are inequivalent.

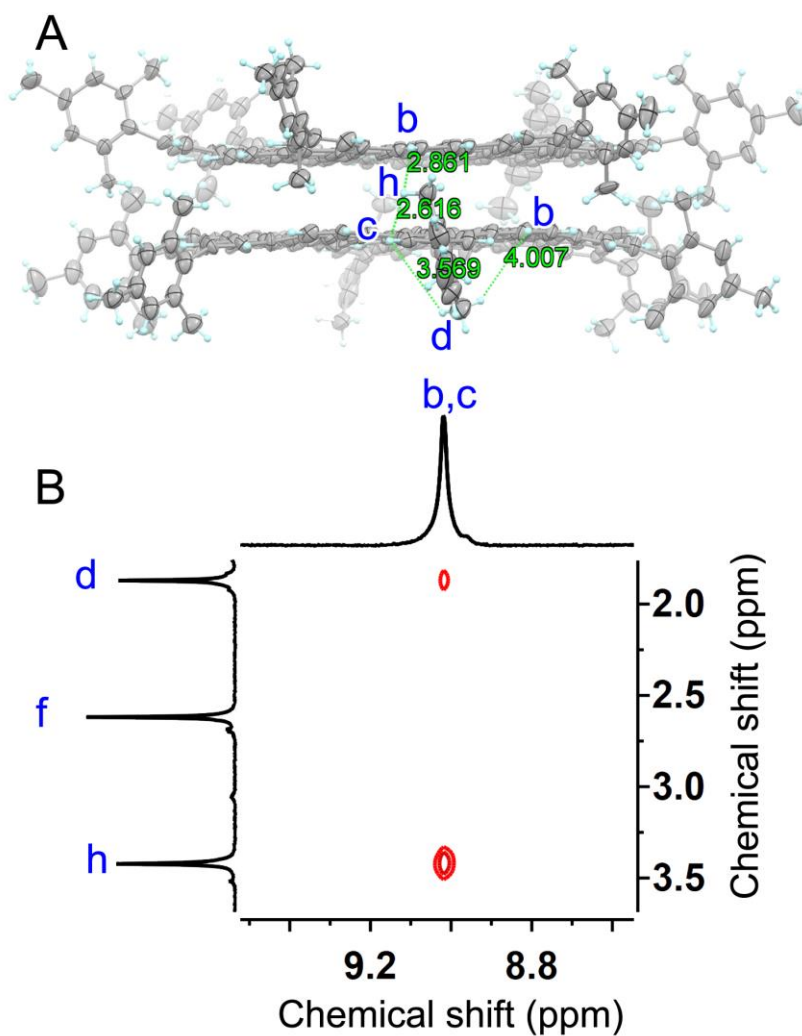


Fig. S8. H...H proximity in 1. (A), Typical H...H proximity between hydrogens of methyl at the mesityl groups and hydrogens at the periphery of inner core found in **1**. The interlayer and intralayer H...H proximity are represented as green dashed lines. (B), Expanded 2D NOESY of **1**, showing the protons coupling.

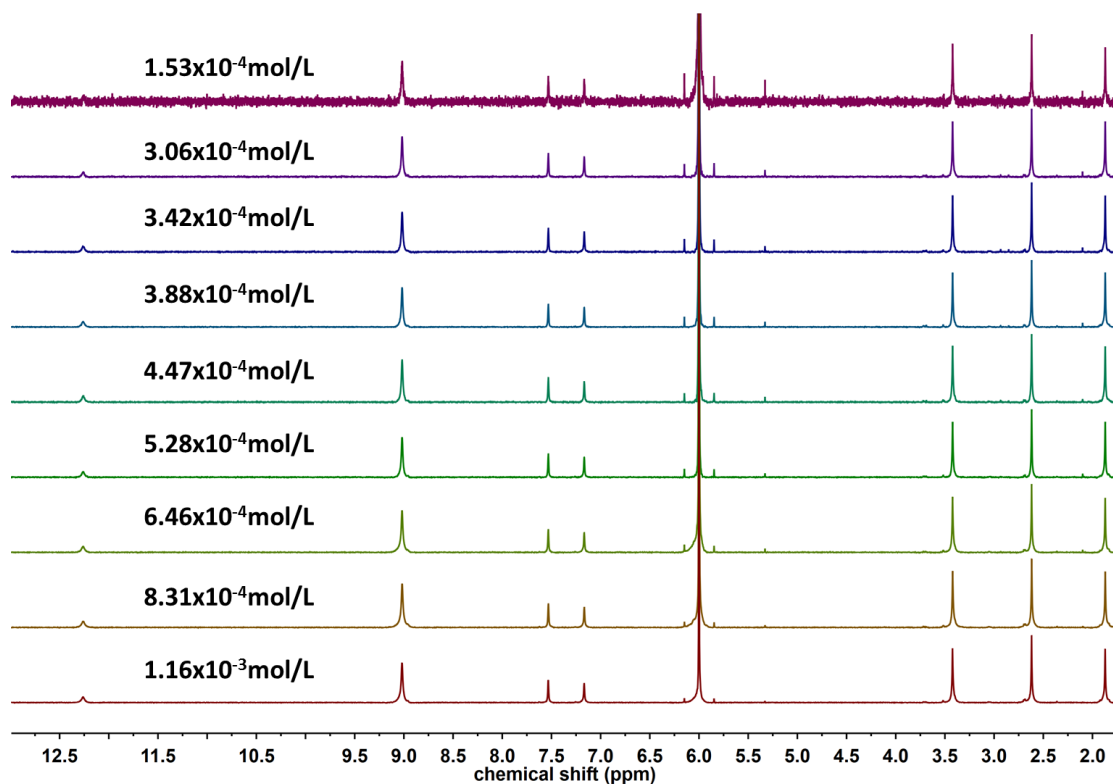


Fig. S9. ^1H NMR spectra of 1 in $\text{C}_2\text{D}_2\text{Cl}_4$ at different concentrations.

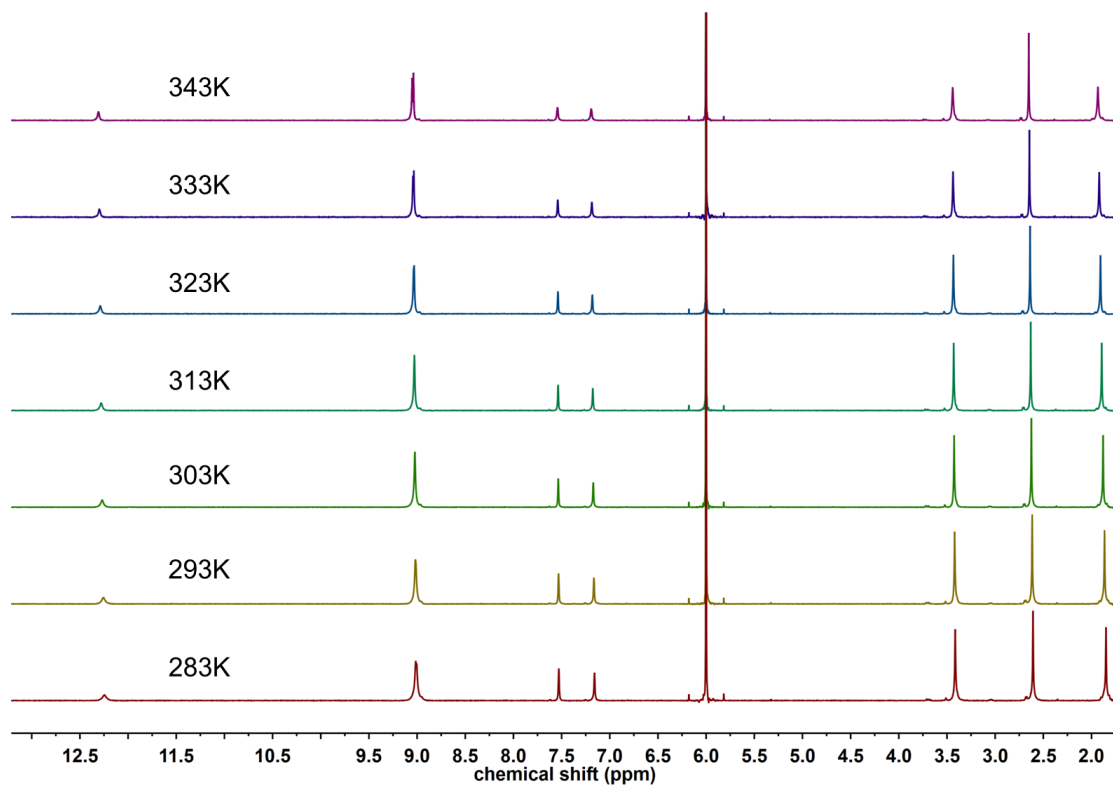


Fig. S10. ^1H NMR spectra of 1 in $\text{C}_2\text{D}_2\text{Cl}_4$ at different temperatures.

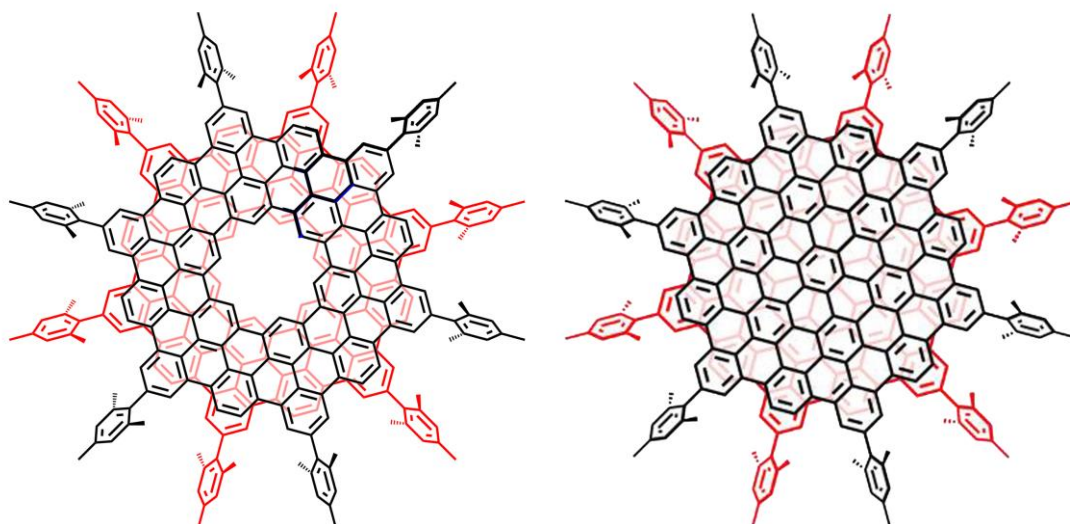


Fig. S11. Structure of 1 (left) and 2 (right).

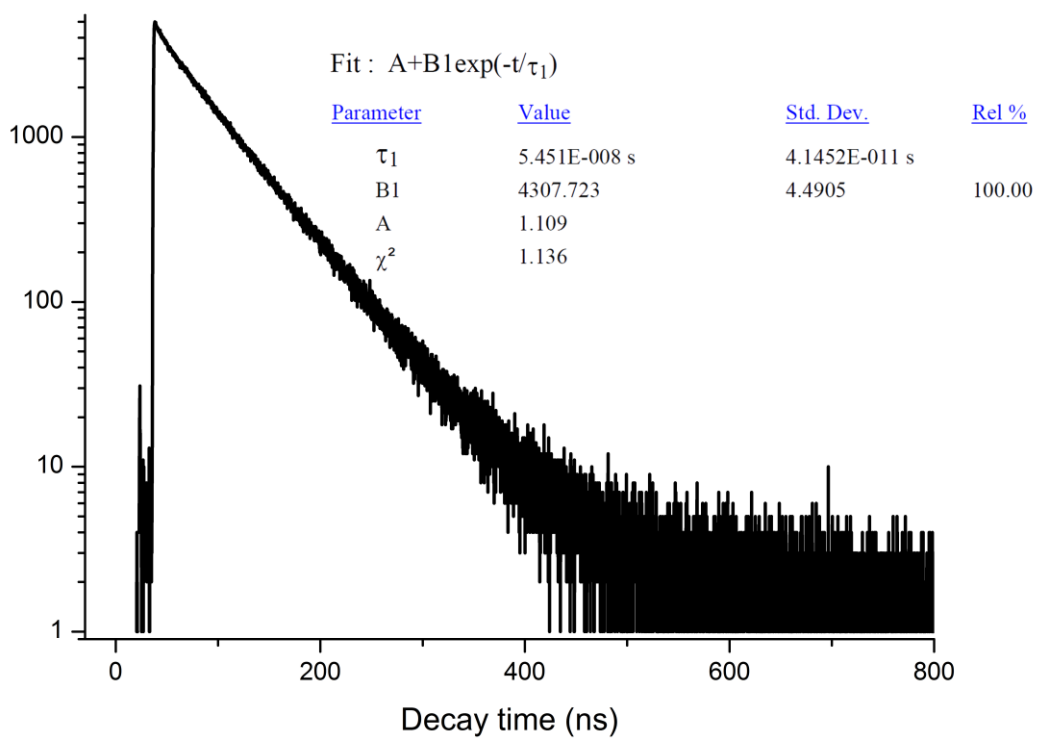


Fig. S12. Time-resolved fluorescence spectrum of 1. The TRPL spectrum was acquired and monitored at 512 nm in a dichloromethane solution.

Table S1. Ultraviolet-visible absorption parameters of 1 and 2.

Compound	α band	p band	β band	Optical gap ^a
1	496 nm (2.50 eV)	454 nm (2.73 eV)	421 nm (2.94 eV)	2.50 eV
2	644 nm (1.93 eV)	588 nm (2.11 eV)	539 nm (2.30 eV)	1.93 eV

a. The optical gap was calculated based on the α band of the spectra.