

## Supporting Information

# U-Shaped Stereoscopic Design Strategy Toward N-Doped Nanographene Segment

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## Supporting Information

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## Instrumentation

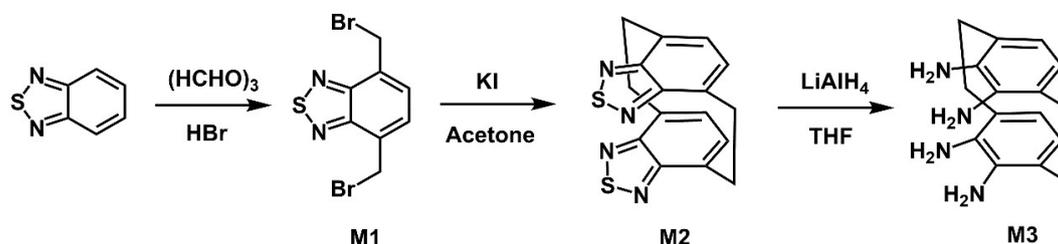
Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400, Bruker AVANCE NEO 600 spectrometer in CDCl<sub>3</sub>. Chemical shifts were reported in parts per million (ppm) and referenced to residual CHCl<sub>3</sub> (7.26 ppm) for <sup>1</sup>H NMR, and to CDCl<sub>3</sub> (77.16 ppm) for <sup>13</sup>C NMR. The following abbreviations were used for multiplicities: s = singlet, d = doublet, dd = double of doublets, t = triplet, m = multiplet. High resolution mass spectrometry (HRMS) was performed via atmospheric pressure chemical ionization (APCI) on an AB Sciex liquid chromatography-quadrupole time of flight tandem mass spectrometry (LC-Q-TOF-MS) with dichloromethane (DCM) as the solvent. Ultraviolet–visible (UV-Vis) absorption spectra were measured on a Perkin-Elmer Lambda 950 spectrophotometer at room temperature. Photoluminescence (PL) spectra were recorded on a Horiba FL3-111 spectrofluorometer. The electrochemical measurements were carried out in anhydrous DCM containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte (scan rate: 10 mV s<sup>-1</sup>) under argon atmosphere on a CHI600E electrochemical analyzer. A three-electrode system with glassy carbon as the working electrode, platinum wire as the reference electrode, another platinum wire as counter electrode was applied. The potential was calibrated against ferrocene/ferrocenium couple. Density functional theory (DFT) calculations were performed using the Gaussian 16 program<sup>1</sup> with the B3LYP hybrid functional<sup>2,3</sup> and basis set 6-31G(d) for the ground state geometry optimization. The single crystals of **BPQ** were obtained by slow evaporation of DCM in solution with concentration of ~0.5 mg/mL in NMR tube. X-ray crystallographic data for the molecules were collected on a Bruker D8 VENTURE dual wavelength Mo/Cu diffractometer. The crystal was kept at 194.0 K during data collection. Using Olex2<sup>4</sup>, the structure was solved with the SHELXT<sup>5</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>5</sup> refinement package using Least Squares minimisation. All the hydrogen atoms were omitted for clarity.

## Reagents and Synthesis

2,7-di-*tert*-butylpyrene-4,5-dione<sup>6</sup> and syn-[2.2](4,7)Benzothiadiazolophane **M2**<sup>7</sup> were prepared according to the reported procedures. All starting chemicals, unless otherwise specified, were purchased from Alfa Aesar or Sigma-Aldrich and used as received.

Solvents were purified by normal procedure before use. The other materials were common commercial level and used as received.

Scheme S1. The synthesis of M3



#### 4,7-bis(bromomethyl)benzo[c][1,2,5]thiadiazole (**M1**)

To a 1-neck, 250 mL round bottom flask equipped with a magnetic stir bar and condenser was added 2,1,3-benzothiadiazole (5.00 g, 36.7 mmol), hydrobromic acid (48 wt% in water, 100 mL). 1,3,5-Trioxane (16.6 g, 184 mmol) and tetra-*n*-octylammonium bromide (2.00 g, 3.66 mmol) were added to the flask while stirring the mixture. The reaction was heated to reflux and stirred for 16 hours. The reaction was cooled to room temperature and the precipitate was filtered, washed with water then ethanol and dried under reduced pressure. The resulting off-white solid was further purified using silica gel column chromatography (eluent: dichloromethane/hexanes = 1:3, v/v), yielding **M1** as a white crystalline solid (10.9 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δppm = 7.63 (s, 2H), 4.97 (s, 4H).

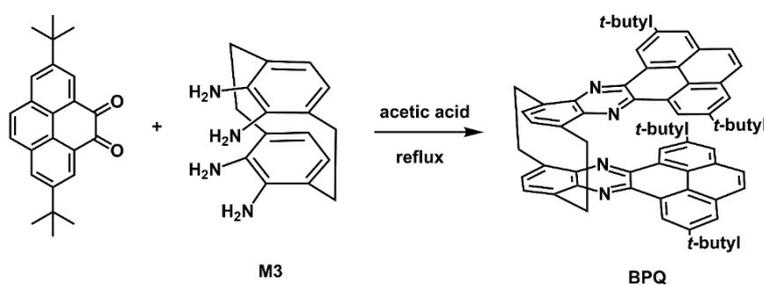
#### syn-[2.2](4,7)Benzothiadiazolophane (**M2**)

A mixture of 4,7-bis(bromomethyl)benzo[c][1,2,5]thiadiazole (**M1**) (322 mg, 1.00 mmol), KI (1.66 g, 10.0 mmol), and acetone (25 mL) was refluxed for 18 h with stirring. After cooling, the solvent was removed under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added to the residue. The resulting precipitate was filtered and the filtrate was concentrated under reduced pressure. The concentrate was separated by silica gel column chromatography (eluent: dichloromethane/hexanes = 1:3, v/v) to give syn-isomer **M2** as yellow crystal (14.3 mg, 9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δppm = 6.80 (s, 4H), 4.16 (dd, 4H, J<sub>1</sub> = 13.16 Hz, J<sub>2</sub> = 4.08 Hz), 3.32 (dd, 4H, J<sub>1</sub> = 13.16 Hz, J<sub>2</sub> = 4.08 Hz).

### M3

syn-[2.2](4,7)Benzothiadiazolophane (**M2**) (32.4 mg, 0.100 mmol) was dissolved in deaerated THF (20 mL) under an argon atmosphere and stirred at 0 °C. Then LiAlH<sub>4</sub> (1.00 mL, 1.0 M in THF, 1.00 mmol) was slowly added. The mixture was heated to 60 °C for overnight. After cooling to room temperature, the reaction mixture was quenched with aqueous NaOH solution. The above solution was filtered through a pad of Celite and the filtrate was extracted with DCM (10 mL × 3). The combined organic layers were collected and dried over anhydrous MgSO<sub>4</sub> (s), filtered, and concentrated to dryness. **M3** was used directly for the next step without further purification. Mp > 300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δppm = 6.06 (s, 4H), 3.37 (dd, 4H, J<sub>1</sub> = 13.25 Hz, J<sub>2</sub> = 4.09 Hz), 2.89 (dd, 4H, J<sub>1</sub> = 13.25 Hz, J<sub>2</sub> = 4.09 Hz). <sup>13</sup>C NMR(CDCl<sub>3</sub>, 600 MHz): δppm = 157.30, 132.19, 128.31, 30.75. HRMS(APCI): *m/z* calcd for C<sub>16</sub>H<sub>21</sub>N<sub>4</sub> [M+H]<sup>+</sup>, 269.1766, found 269.1765.

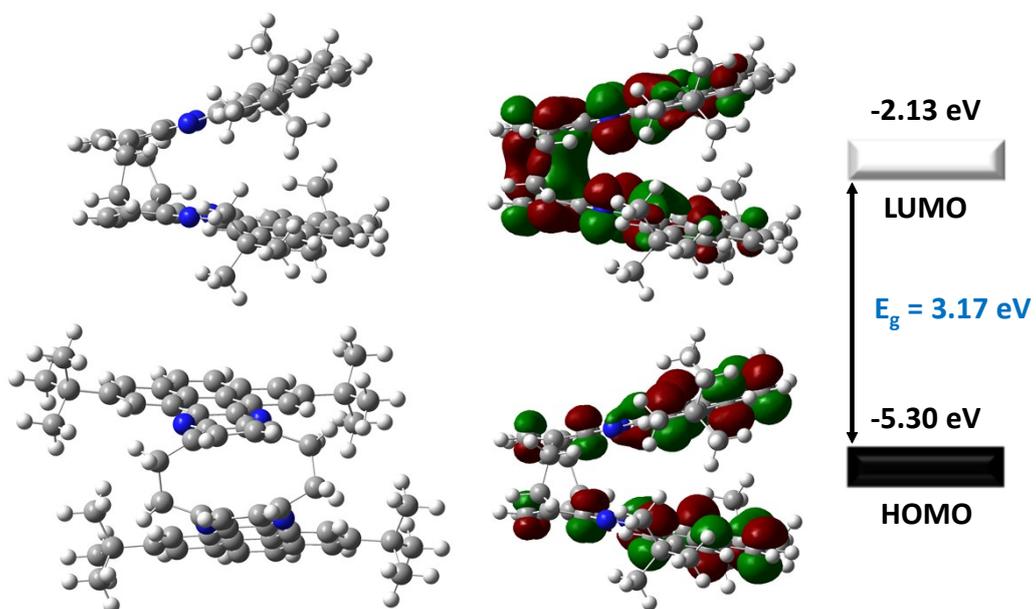
Scheme S2. The synthesis of BPQ



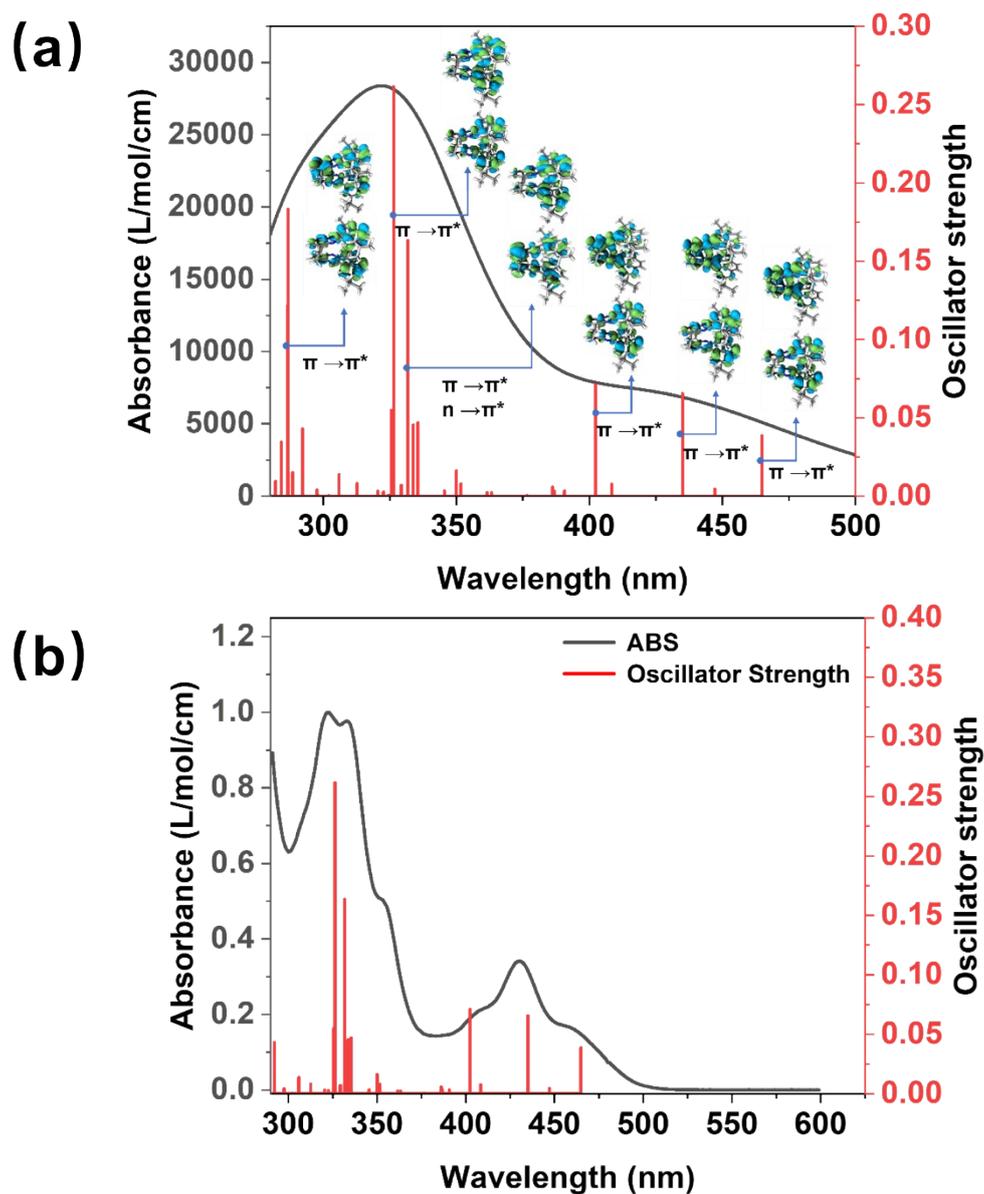
### BPQ

2,7-di-*tert*-butylpyrene-4,5-dione (344 mg, 1.00 mmol) and **M3** (134 mg, 0.500 mmol) were dissolved in acetic acid (20 mL), and the mixture was heated to reflux under argon for 24 h. After the mixture cooling to room temperature, all the solvents were removed under vacuum. The residues were elute by silica gel column chromatography (eluent: dichloromethane/hexanes = 1:3, v/v, R<sub>f</sub> = 0.35, yellow fluorescence) to obtain the **BPQ** as bright yellow powder (131 mg, 30%). Mp > 300 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δppm = 8.96 (s, 4H), 7.73 (s, 4H), 7.55 (s, 4H), 7.22 (s, 4H), 4.85 (d, 4H, J = 6.24 Hz), 3.39 (d, 4H, J = 6.24 Hz), 1.39 (s, 36H). Attached proton test (APT) <sup>13</sup>C (CDCl<sub>3</sub>, 600 MHz): δppm = 148.19, 142.54, 140.72, 138.72, 132.87, 130.26, 128.28, 126.40, 125.16, 123.31, 120.23, 35.11, 31.86, 31.73. HRMS(APCI): *m/z* calcd for C<sub>64</sub>H<sub>61</sub>N<sub>4</sub> [M+H]<sup>+</sup>, 885.4896, found 885.4895.

## DFT Results

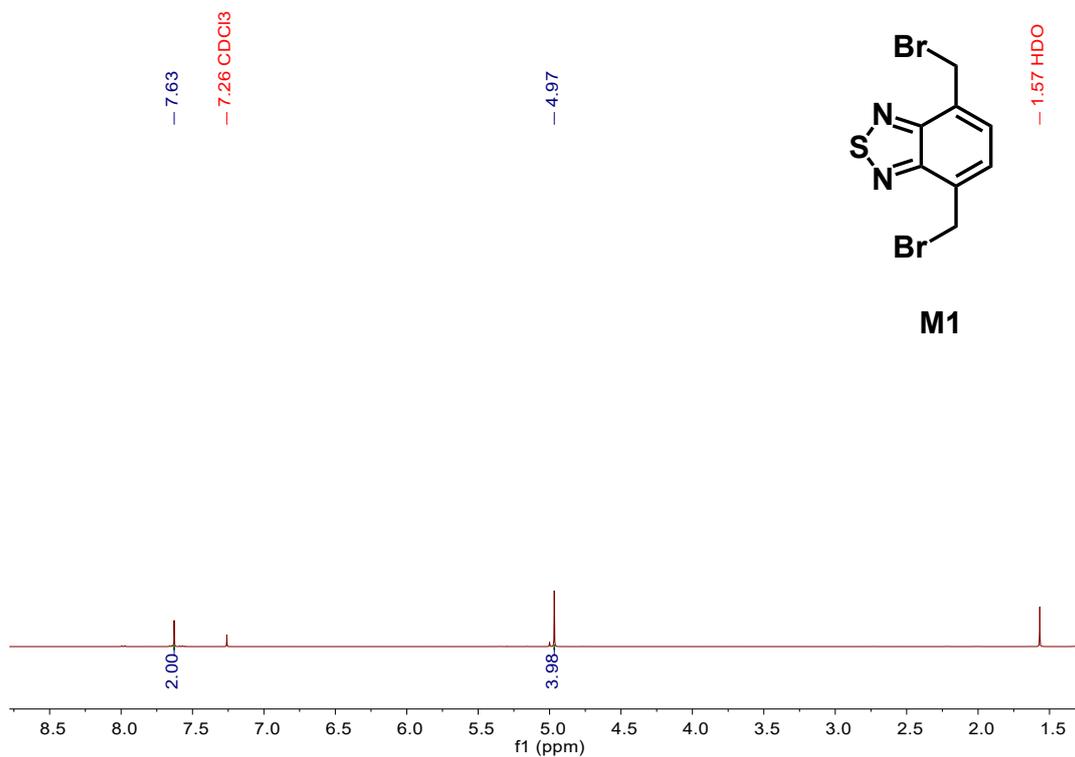


**Fig. S1** DFT calculated molecular orbitals and energy diagrams of BPQ at the B3LYP/6-31G(d) level (the LUMO and HOMO: the lowest unoccupied and highest occupied molecular orbitals).

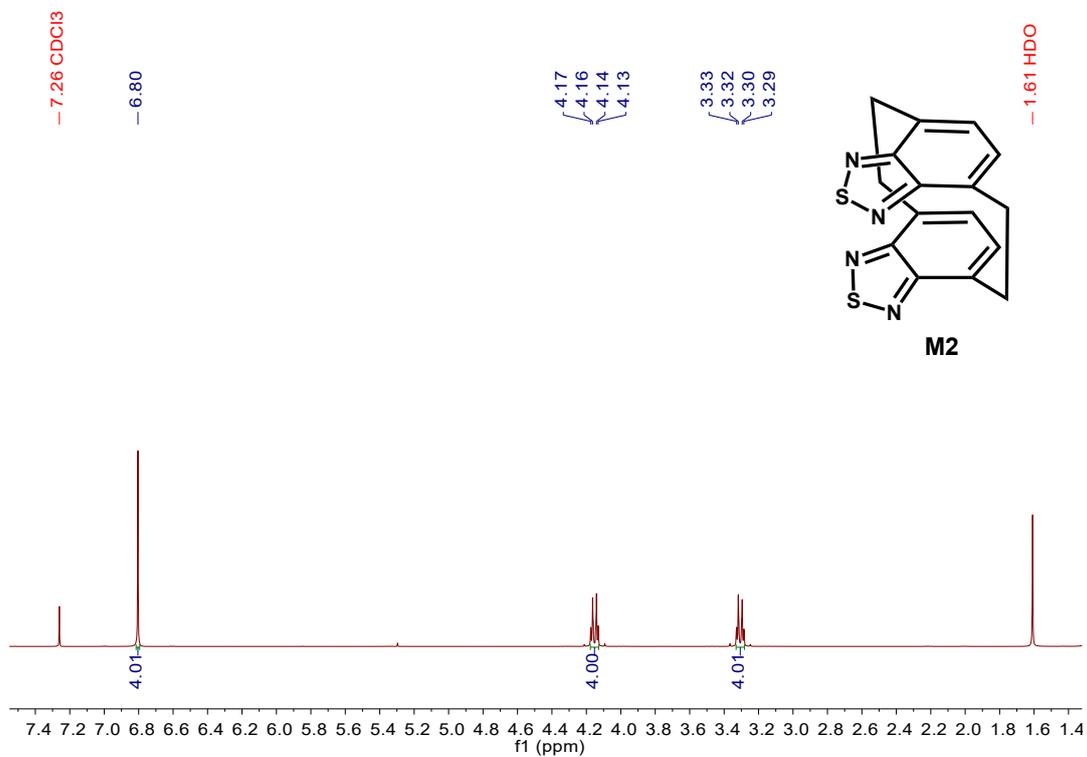


**Fig. S2** TDDFT-calculated absorption spectra of BPQ along with the oscillator strengths. (a) The calculated results of the UV-visible absorption spectrum fitted with corresponding energy level transitions. (b) Comparison between the calculated results and the experimental UV-visible absorption spectrum.

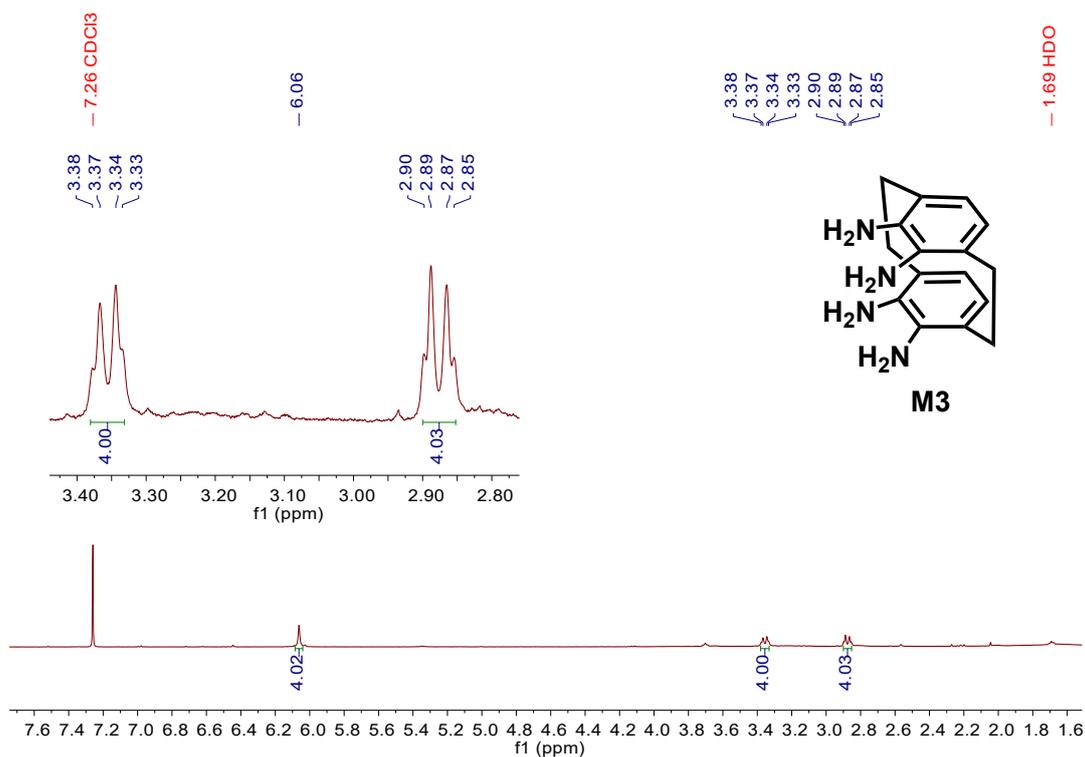
## NMR Spectra



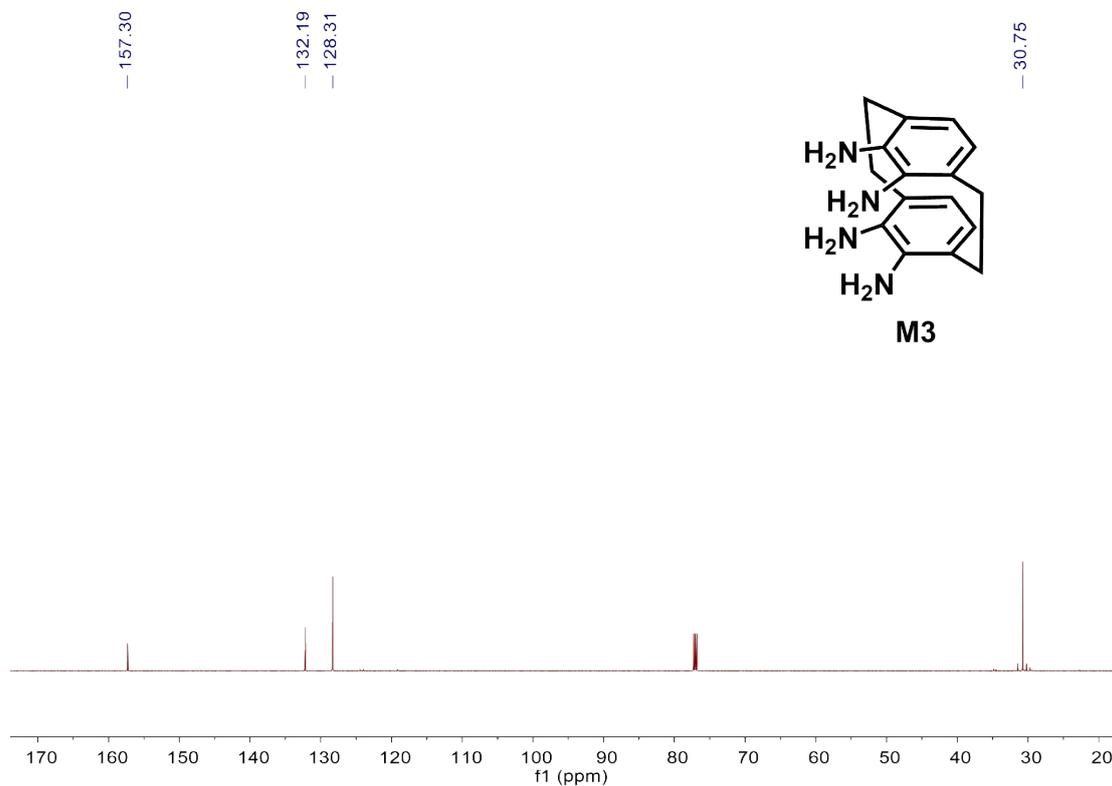
**Fig. S3** The <sup>1</sup>H NMR spectrum of compound M1 in CDCl<sub>3</sub> on 400 MHz.



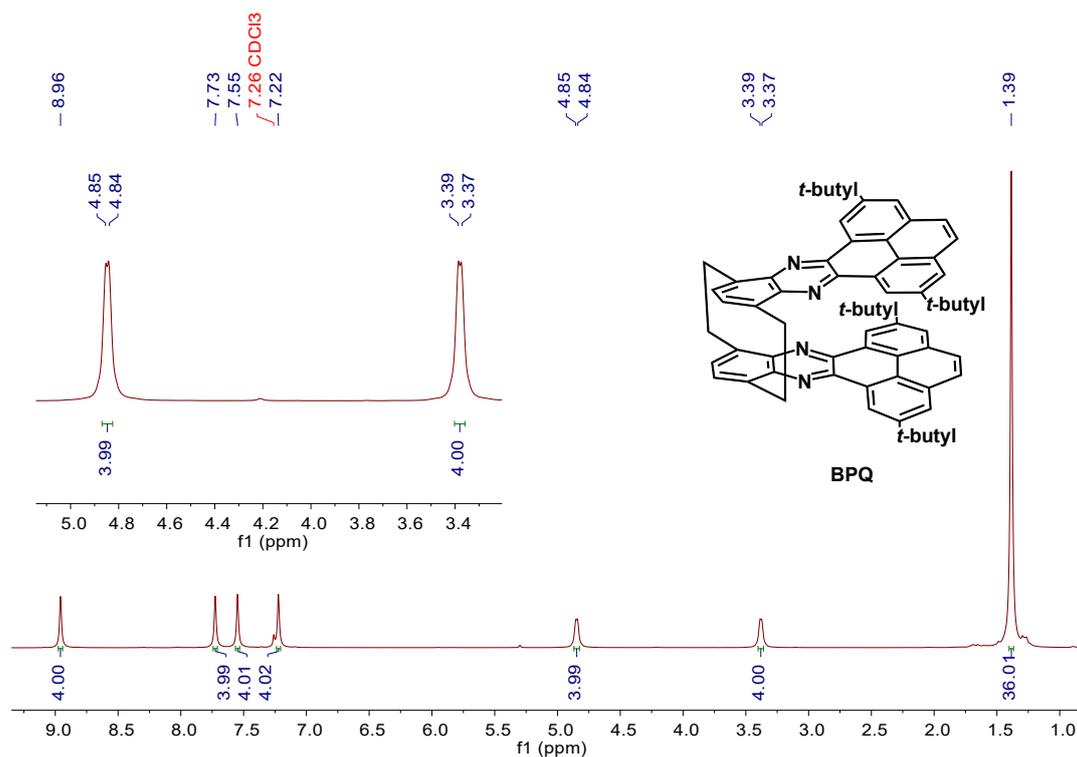
**Fig. S4** The <sup>1</sup>H NMR spectrum of compound M2 in CDCl<sub>3</sub> on 400 MHz.



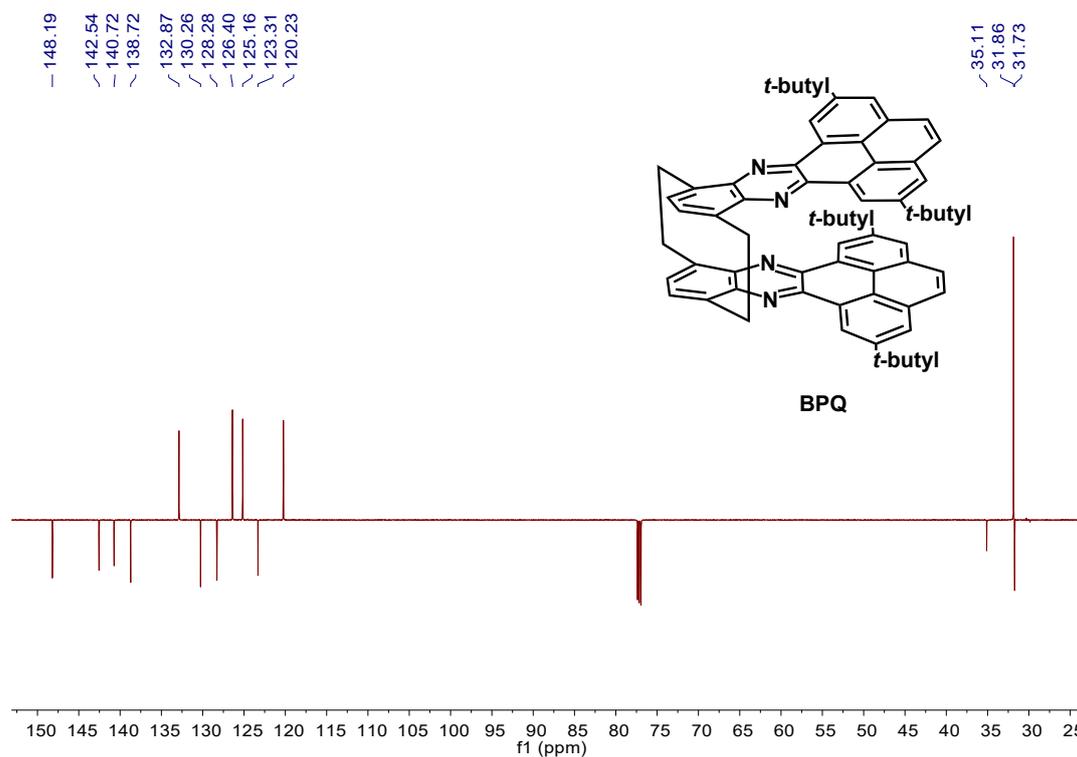
**Fig. S5** The <sup>1</sup>H NMR spectrum of compound M3 in CDCl<sub>3</sub> on 400 MHz.



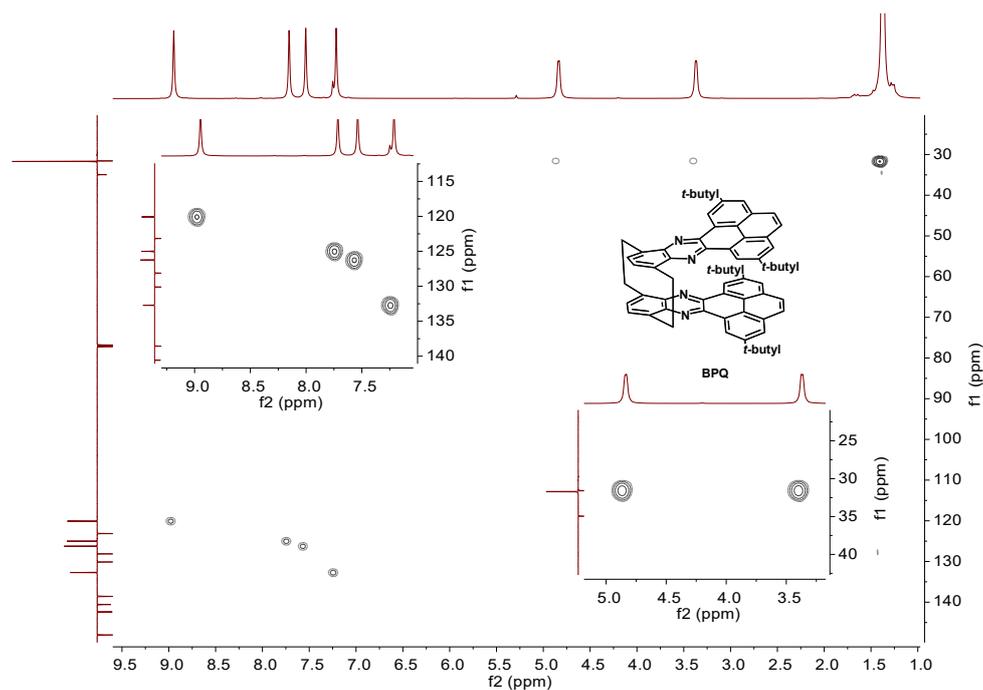
**Fig. S6** The <sup>13</sup>C NMR spectrum of compound M3 in CDCl<sub>3</sub> on 600 MHz.



**Fig. S7** The  $^1\text{H}$  NMR spectrum of compound BPQ in  $\text{CDCl}_3$  on 600 MHz.

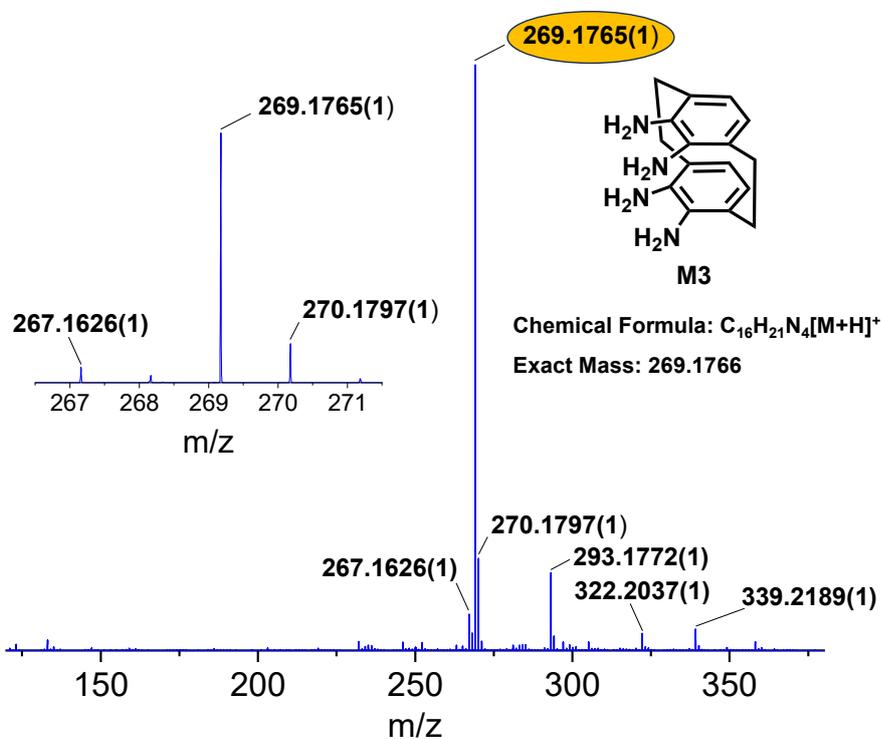


**Fig. S8** The attached proton test (APT)  $^{13}\text{C}$  NMR spectrum of compound BPQ in  $\text{CDCl}_3$  on 600 MHz.

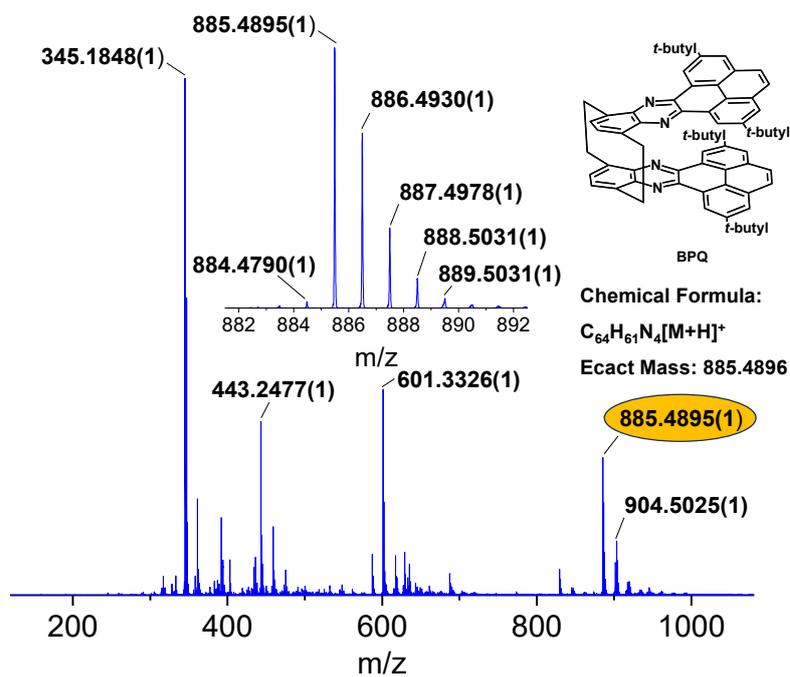


**Fig. S9** The 2D  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear single quantum coherence (HSQC) NMR spectrum of BPQ in  $\text{CDCl}_3$  on 600 MHz.

## HRMS Spectra

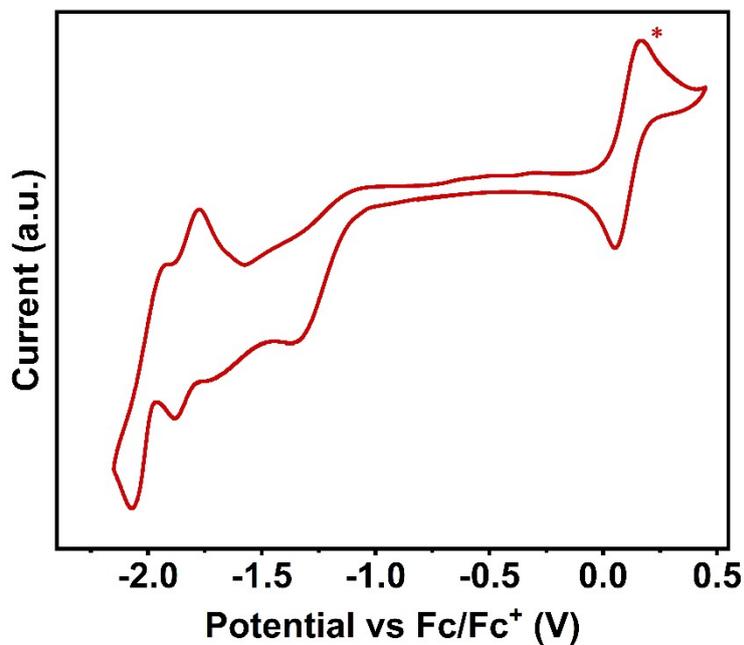


**Fig. S10** High-resolution mass spectrum of  $\text{M3}([\text{M}+\text{H}]^+)$ .



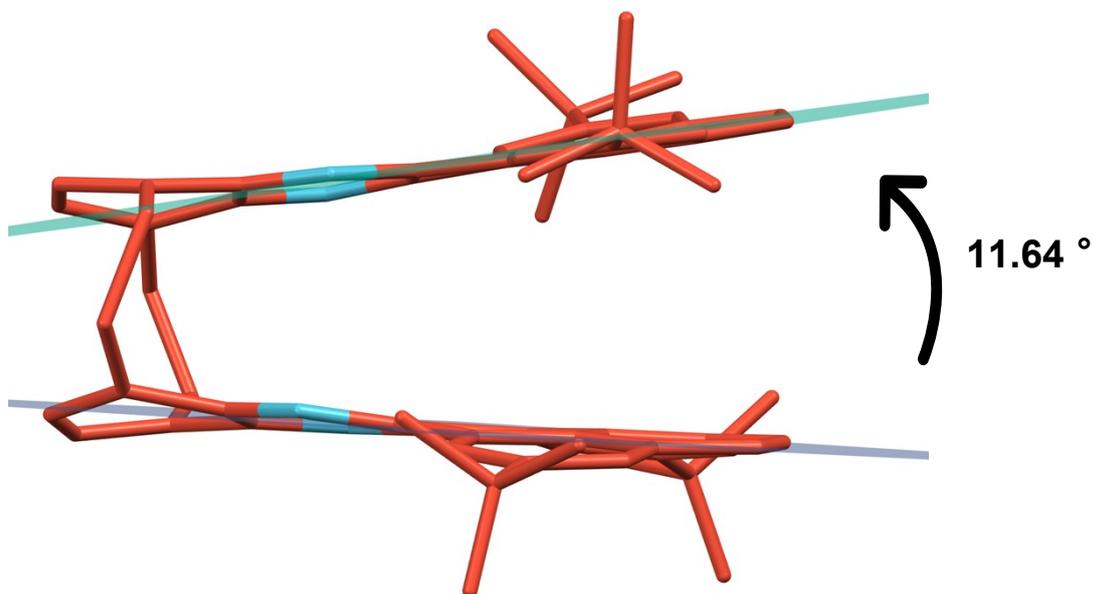
**Fig. S11** High-resolution mass spectrum of BPQ( $[M+H]^+$ ).

## Electrochemical Measurement

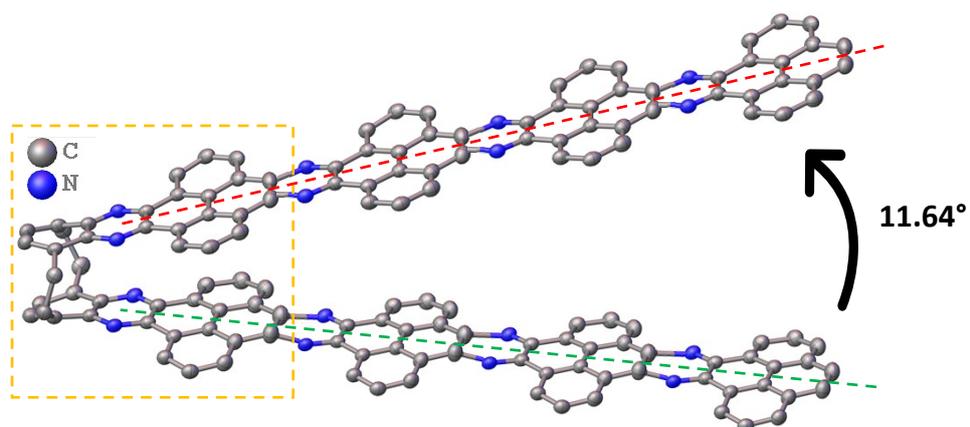


**Fig. S12** Cyclic voltammogram of BPQ in THF with ferrocene (ferrocene peaks are indicated by red star and occur at positive potential) as an internal standard, the energy of  $Fc/Fc^+$  was assumed as  $-4.8$  eV relative to vacuum.

## Single Crystal X-Ray Analysis

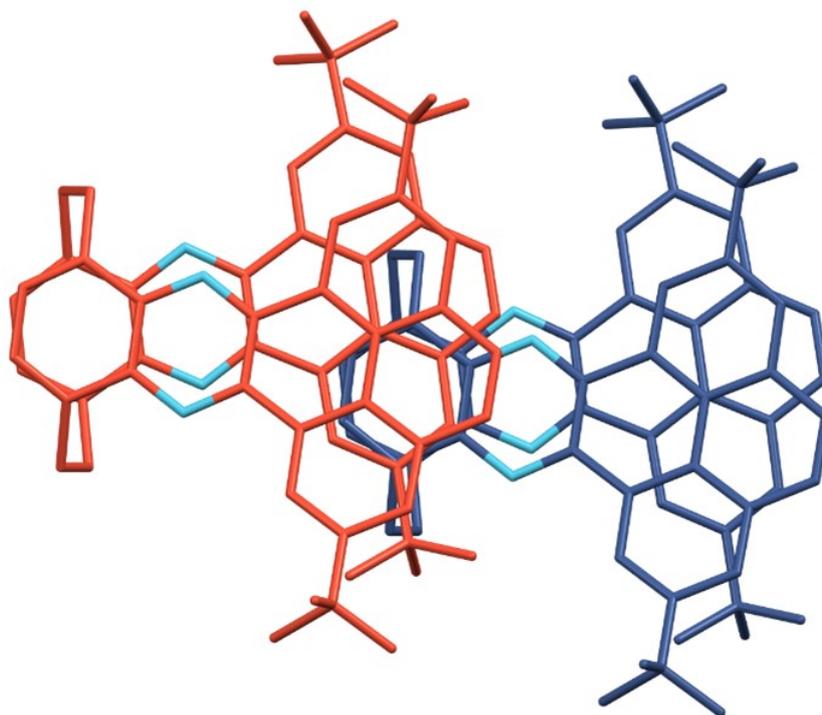


**Fig. S13** Dihedral angle of BPQ.

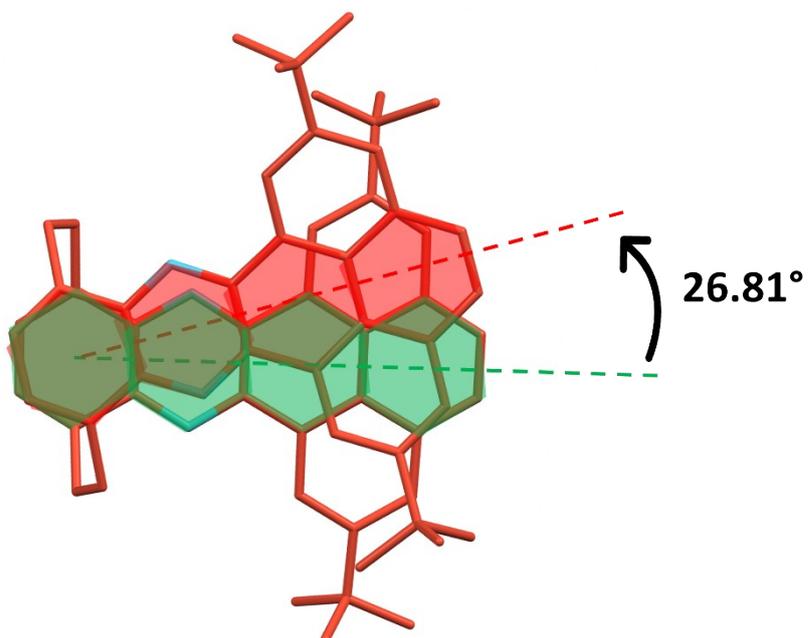


**N-Doped Nanographene Segment**

**Fig. S14** BPQ can be described as a segment of N-doped nanographene.



**Fig. S15** The  $\pi$ - $\pi$  overlap of BPQ.



**Fig. S16** The displacement of the upper and lower acene frameworks containing the pyrene skeleton.

**Table S1.** Crystal data and structure refinement for BPQ.

Identification code	<b>BPQ</b>
CCDC number	2322933
Empirical formula	C <sub>64</sub> H <sub>60</sub> N <sub>4</sub>
Formula weight	885.16
Temperature/K	194.00
Crystal system	monoclinic
Space group	C2/c
a/Å	36.4386(8)
b/Å	9.7054(3)
c/Å	30.3886(7)
$\alpha$ /°	90
$\beta$ /°	110.4310(10)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	10070.9(5)
Z	8
$\rho_{\text{calc}}$ /g/cm <sup>3</sup>	1.168
$\mu$ /mm <sup>-1</sup>	0.515
F(000)	3776.0
Crystal size/mm <sup>3</sup>	0.13 × 0.12 × 0.1
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\Theta$ range for data collection/°	6.208 to 159.886
Index ranges	-43 ≤ h ≤ 45, -12 ≤ k ≤ 12, -37 ≤ l ≤ 23
Reflections collected	50391
Independent reflections	10415 [R <sub>int</sub> = 0.0811, R <sub>sigma</sub> = 0.0545]
Data/restraints/parameters	10415/144/688
Goodness-of-fit on F <sup>2</sup>	1.075
Final R indexes [I >= 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0711, wR <sub>2</sub> = 0.1930
Final R indexes [all data]	R <sub>1</sub> = 0.1057, wR <sub>2</sub> = 0.2310
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.37

## References

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