Turning on the Biradical State of Tetracyano- Perylene and Quaterrylenequinodimethanes by Incorporation of Additional Thiophene Rings

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1. Experimental section

1.1. General

All reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous *N*, *N*-dimethylformaldehyde (DMF) was distilled from CaH_2. Anhydrous toluene and THF were distilled from sodium-benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ or THF-d_8 on Bruker DPX 300 or DRX 500 NMR spectrometers with tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. MALDI-TOF mass spectra (MS) were recorded on a Bruker Autoflex instrument using anthracene-1,8,9-triol as matrix. EI mass spectra were recorded on Agilent 5975C DIP/MS mass spectrometer. Steady-state UV/Vis-NIR absorption were recorded on a Shimadzu UV-1700 and UV-3600 spectrometer. The solvents used for UV/Vis-NIR measurements are of HPLC grade (Merck). The electrochemical measurements were carried out in anhydrous methylene chloride with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at room temperature under the protection of nitrogen. A gold stick was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3M KCl solution) was used as reference electrode. The potential was externally calibrated against the ferrocene/ferrocenium couple. Continuous wave X-band ESR spectra were obtained with a Bruker ELEXSYS E500 spectrometer using a variable temperature Bruker liquid nitrogen cryostat.

A Quantum Design 7 Tesla SQUID-VSM system was available for the magnetic measurements in this work. Powder sample with a weight of 5-10 mg was sealed in a plastic capsule. Magnetic moment was measured in the temperature range of 5 to 300 K. The empty plastic capsule exhibited diamagnetic and its magnetic moment was measured for correction. The magnetic susceptibility was fitted with Bleaney-Bowers equation ($\chi = \frac{N\beta^2 g^2}{3kT}\left[1+\frac{1}{3}\exp(\frac{J_{s-t}}{kT})\right]^{-1}$) after correction of diamagnetic signal of

plastic capsule and sample holder and paramagnetic contamination (for example free radical).

Raman spectra were measured using a Raman accessory kit (FRA/106–S) of a Bruker Equinox 55 FT–IR interferometer. A continuous–wave Nd–YAG laser working at 1064 nm was employed for excitation, at a laser power in the sample not exceeding 30 mW. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back–scattering configuration with a standard spectral resolution of 4 cm^{-1}. 2000 scans were averaged for each spectrum. A variable-temperature cell Specac P/N 21525, with interchangeable pairs of quartz windows, was used to record the Raman spectra at different temperatures. The variable temperature cell consists of a surrounding vacuum jacket (0.5 Torr), and combines a refrigerant Dewar and a heating block as the sample holder. It is also equipped with a copper constantan thermocouple for temperature monitoring between -180 and 100 ^{o}C. Samples were inserted into the heating block part or the Dewar/cell holder assembly in the form of pure solids dispersed in KBr pellets, and Raman spectra were recorded after waiting for thermal equilibrium in the sample. The samples in KBr pellets were prepared in an oxygen and water-free bag.

The femtosecond time-resolved transient absorption spectrometer used for this study consisted of a femtosecond optical parametric amplifier (Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical detection system. The generated OPA pulses had a pulse width of ~100 fs and an average power of 1 mW in the range 450 to 800 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm thick) by focusing of small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by miniature spectrograph (OceanOptics, USB2000+). To obtain the

time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses were used excite samples and to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7^o) using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation fwhm in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

The two-photon absorption spectrum was measured in the NIR region using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a repetition rate of 3 kHz generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). After passing through a 10 cm focal length lens, the laser beam was focused and passed through a 1 mm quartz cell. Since the position of the sample cell could be controlled along the laser beam direction (z axis) using the motorcontrolled delay stage, the local power density within the sample cell could be simply controlled under constant laser intensity. The transmitted laser beam from the sample cell was then detected by the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 60 GW cm^{-2}. For a Gaussian beam profile, the nonlinear absorption coefficient can be obtained by curve fitting of the observed open-aperture traces $T(z)$ with the following equation:

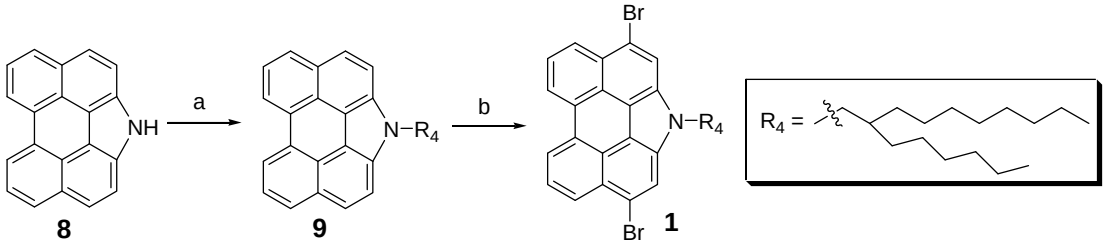
$$T(z)=1-\frac{\beta I_0(1-e^{-\alpha_0 l})}{2\alpha_0[1+(z/z_0)^2]}$$

where α_0 is the linear absorption coefficient, l is the sample length, and z_0 is the diffraction length of the incident beam. After the nonlinear absorption coefficient has been obtained, the TPA cross section $\sigma^{(2)}$ of one solute molecule (in units of GM, where 1 GM = 10^{-50}cm^4 s photon^{-1} molecule^{-1}) can be determined by using the following relationship:

$$\beta = \frac{10^{-3}\sigma^{(2)}N_A d}{h\nu}$$

where N_A is the Avogadro constant, d is the concentration of the compound in solution, h is the Planck constant, and v is the frequency of the incident laser beam.

Compounds **4** was prepared according to literatures as indicated in main text. Compound **1** was prepared according to Scheme S1. Treatment of the *N*-annulated perylene **8** with 2-hexyldecyl bromide afforded compound **9**. Bromination of **9** with two equivalent *N*-bromosuccinimide (NBS) gave the dibrominated NP **1** in 94% yield.



Scheme S1. Synthesis of compound **8**. *Reaction conditions*: a) R_4Br, KOH, KI, THF, (n-Bu)$_4$NBr, 65 ºC, 24h, 99%; b) 2 equiv NBS, DCM/DMF, 0 ºC-25 ºC, overnight, 90%.

1.2. Synthetic procedure and characterization data

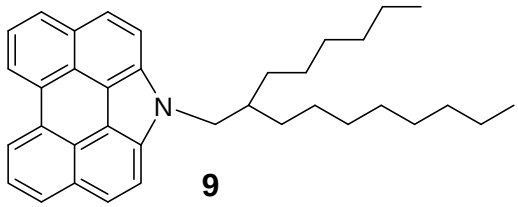
General synthesis of the dithieno-NP and NP dimer by Stille coupling

A mixture of dibromo- oligo(*N*-annulated perylenes) **1** or **4** (1.54 mmol) and tributyl-(thiophen-2-yl)stannane (1.73 g, 4.63 mmol), Ph(PPh$_3$)$_4$ (87 mg, 0.08 mmol) and toluene/DMF (100 mL, 4 : 1, v/v) was heated at 80 °C under nitrogen atmosphere for 24 h. After cooling, water (80 mL) was added and the mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with water (4 x 50 mL) and saturated brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was then purified by column chromatography (silica gel) to give

the solid product.

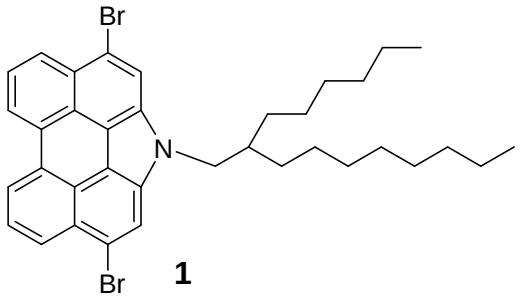
*General procedure for the synthesis of dibromo-derivatives **1,3**,* and ***6***

To the solution of NP oligomers **8, 2** or **5** (0.50 mmol) in DCM (200 mL) was added NBS (1.05 mmol) solution in DMF (3 mL). The mixture was stirred at 0 °C for 0.5 h, then warmed to room temperature and stirred overnight. The reaction mixture was quenched with water (50 mL). The organic layer was washed with water (3 x 100 mL) to remove DMF, and then washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was washed with a large amount of methanol (300 mL) to give a pure yellow solid product.



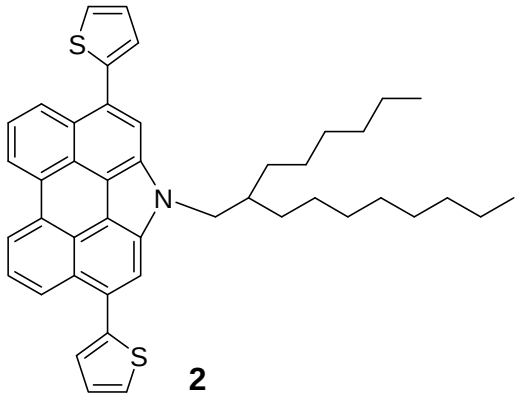
9

A mixture of 6*H*-phenanthro [1,10,9,8-c,d,e,f,g] carbazole (**8**, 500 mg, 1.88 mmol), KOH (220 mg, 2.38 mmol), 2-hexyldecyl bromide (863 mg, 2.38 mmol), a small amount of KI (16 mg, 0.09 mmol) and tetrabutylammonium bromide (2 mg) in dry THF (50 mL) was stirred at 65 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexane) to give a yellow oil product (920 mg, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.64 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.79-7.87 (m, 4H), 7.64 (d, J = 8.8 Hz, 2H), 4.29 (d, J = 7.3 Hz, 2H), 2.18-2.19 (m, 1H), 1.24-1.37 (m, 24H), 0.91-0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.97, 130.24, 128.63, 124.79, 124.70, 124.26, 123.33, 120.44, 117.11, 113.27, 49.72, 39.84, 31.83, 31.76, 31.70, 29.83, 29.55, 29.46, 29.23, 26.44, 26.67, 22.63, 22.58, 14.10, 14.04. HR-MS (EI, *m*/*z*): caldc for $C_{36}H_{43}N$, 489.3396; found, 489.3390 (error = - 1.1 ppm).



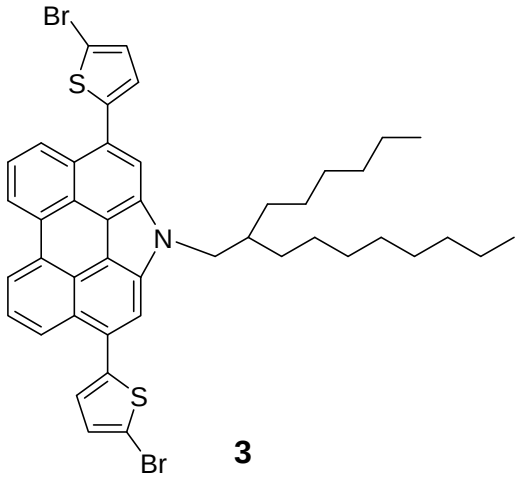
1

Yellow solid; 90% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.15 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.47 (s, 2H), 3.73 (d, *J* = 7.5 Hz, 2H), 1.83-1.84 (m, 1H), 1.17-1.24 (m, 24H), 0.83-0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 130.70, 128.88, 126.95, 124.83, 124.37, 122.87, 121.05, 117.47, 116.23, 115.05, 49.42, 39.45, 31.81, 31.74, 31.50, 31.46, 29.79, 29.50, 29.45, 29.26, 26.26, 22.59, 14.09, 14.05. HR-MS (EI, *m*/*z*): caldc for $C_{36}H_{41}Br_2N$, 645.1606; found, 645.1586 (error = - 3.1 ppm).



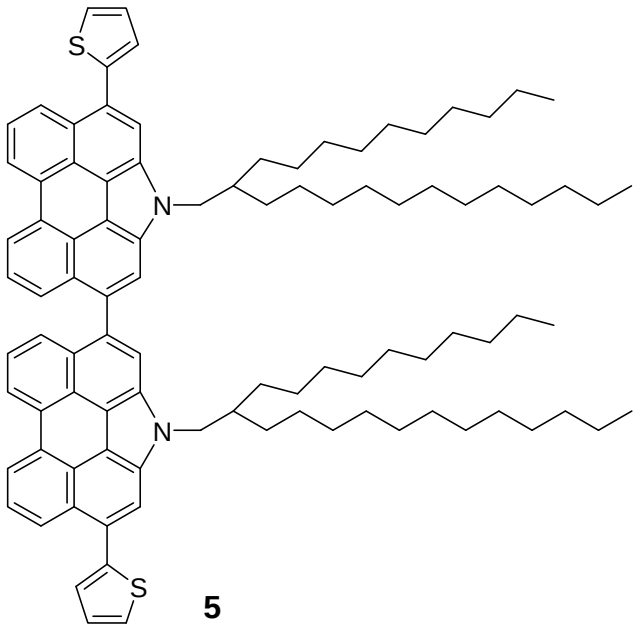
2

Yellow solid; 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.72 (d, *J* = 7.4 Hz, 2H), 8.44 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 2H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.46-7.49 (m, 4H), 7.27-7.29 (m, 2H), 4.57 (d, *J* = 7.3 Hz, 2H), 2.29-2.32 (m, 1H), 1.18-1.40 (m, 24H), 0.78-0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.61, 132.21, 130.55, 129.51, 127.91, 127.48, 126.99, 125.22, 124.93, 124.73, 124.20, 121.22, 117.22, 115.18, 50.05, 39.80, 31.82, 31.76, 31.72, 31.68, 29.91, 29.61, 29.49, 29.23, 26.38, 22.59, 14.07, 14.02. MS (MALDI-TOF, *m*/*z*): 653.4; HR-MS (EI, *m*/*z*): caldc for $C_{44}H_{47}NS_2$, 653.3150; found, 653.3146 (error = - 0.6 ppm).



3

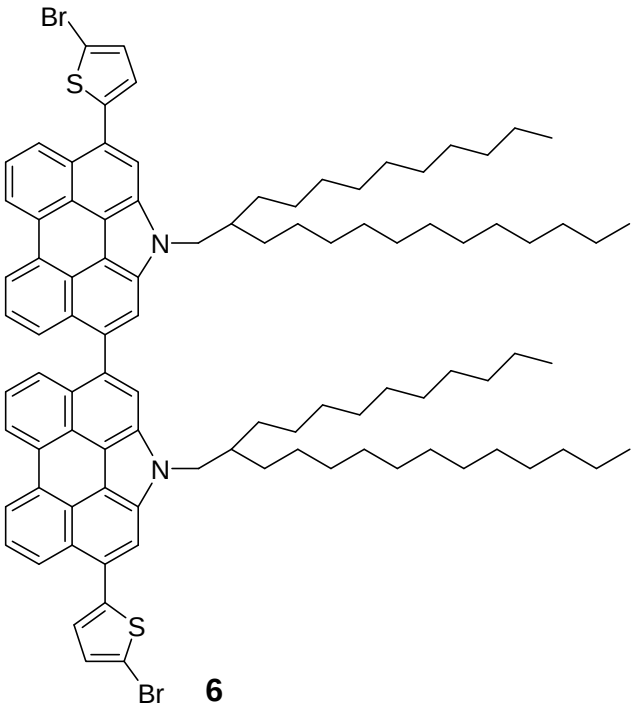
Yellow solid; 87% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (d, J = 7.3 Hz, 2H), 8.41 (d, J = 7.8 Hz, 2H), 7.85 (t, J = 7.0 Hz, 2H), 7.83 (s, 2H), 7.19-7.23 (m, 4H), 4.54 (d, J = 7.4 Hz, 2H), 2.24-2.29 (m, 1H), 1.17-1.38 (m, 24H), 0.80-0.82 (m, 6H); ^{13}C NMR (CS_2/$CDCl_3$, 125 MHz): δ 192.46 (CS_2), 145.11, 132.06, 130.38, 130.27, 128.66, 127.56, 127.17, 125.16, 124.58, 123.85, 121.41, 117.31, 115.02, 111.62, 49.95, 39.83, 31.90, 31.86, 31.75, 31.72, 30.01, 29.71, 29.60, 29.35, 26.48, 22.74, 14.14, 14.10. HR-MS (MALDI-TOF, m/z): caldc for $C_{44}H_{45}Br_2NS_2$, 809.1360; found, 809.1366 (error = + 0.8 ppm).



5

Yellow solid; 71% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.71-8.78 (m, 4H), 8.50 (d, J = 8.3 Hz, 2H), 8.06 (s, 2H), 7.99 (s, 2 H), 7.82-7.91(m, 4H), 7.67 (t, J = 8.1 Hz, 2H),

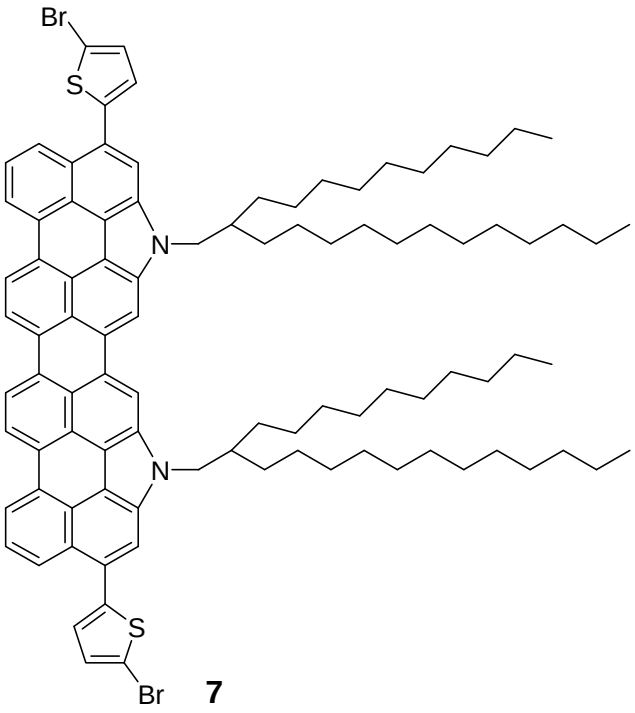
7.50-7.52 (m, 4H), 7.29-7.32 (m, 2H), 4.63 (d, J = 7.3 Hz, 4H), 2.32-2.36 (m, 4H), 1.08-1.42 (m, 80H), 0.81-0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ143.78, 136.77, 132.62, 131.96, 130.71, 129.31, 129.17, 128.00, 127.49, 126.97, 125.15, 124.91, 124.68, 124.64, 124.14, 121.14, 121.01, 117.51, 117.00, 115.55, 115.28, 50.16, 39.93, 31.89, 31.85, 31.73, 29.98, 29.94, 29.69, 29.59, 29.31, 29.27, 26.43, 22.66, 22.62, 14.10. HR-MS (MALDI-TOF, *m*/*z*): caldc for $C_{96}H_{120}N_2S_2$, 1364.8893; found, 1364.8887 (error = + 4.9 pm).



6

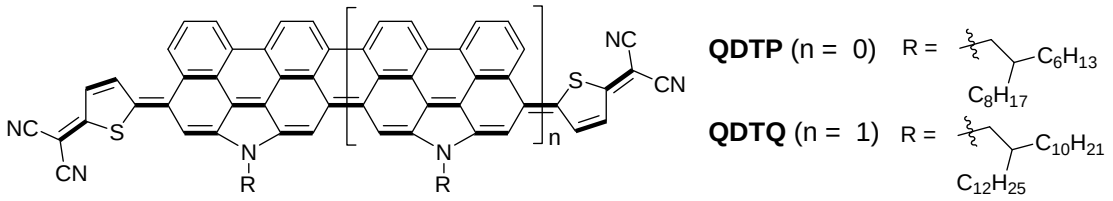
Yellow solid; 82% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.77 (d, J = 7.6 Hz, 2H), 8.72 (d, J = 7.6 Hz, 2H), 8.46 (d, J = 8.4 Hz, 2H), 8.04 (s, 2H), 7.92 (s, 2H), 7.89 (t, J = 8.0 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.67 (t, J = 7.9 Hz, 2H), 7.24 (m, 4H), 4.61-4.63 (m, 4H), 2.33 (m, 2H), 1.17-1.40 (m, 80H), 0.81-0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.43, 136.99, 132.79, 131.77, 130.77, 130.43, 130.34, 129.28, 128.12, 127.75, 127.23, 125.12, 124.99, 124.86, 124.72, 124.65, 123.75, 121.26, 121.16, 117.79, 116.92, 115.52, 115.31, 114.06, 114.33, 50.14, 39.93, 31.89, 31.86, 31.78, 31.71, 29.99, 29.94, 29.70, 29.65, 29.60, 29.36, 29.31, 29.27, 26.42, 26.39, 22.66, 22.62, 14.11. HR-MS (MALDI-TOF, *m*/*z*): caldc for $C_{96}H_{118}Br_2N_2S_2$, 1520.7103; found, 1520.7098

(error = -3.4 pm).



7

A mixture of compound **6** (300 mg, 0.20 mmol), $Sc(OTf)_3$ (520 mg, 1.0 mmol), DDQ (240 mg, 1.0 mmol) in toluene (50 mL) was refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel ($CHCl_3$/Hexane = 1 : 2) to yield the green product (213 mg, 70%). HR-MS (MALDI-TOF, *m*/*z*): caldc for $C_{96}H_{116}Br_2N_2S_2$, 1518.6947; found, 1518.7010 (error = + 4.1 ppm). The ^1H NMR and ^{13}C NMR spectra recorded in various solvents only displayed broad signals due to strong aggregation induced by the π-π stacking between the quaterrylene units as well as enhancement of the stacking effect with the long branch alkyl chains, even though the measurements were done at elevated temperature such as 100 ^oC in $CDCl_2CDCl_2$. The UV-vis-NIR absorption spectrum (Figure S1 in SI) is very similar to our previous reported bis-*N*-annulated quaterrylene analog (see ref. 14 in main text).



To the solution of malononitrile (130 mg, 1.97 mmol) in dry THF (40 mL) was slowly added NaH (60% dispersion in mineral oil, 118 mg, 2.96 mmol) at 0 °C under nitrogen atmosphere, and the mixture was stirred at 0 °C for 0.5 h, then warmed to room temperature and stirred for another 0.5 h. The dibrominated dithienoperylene **3** (200 mg, 0.25 mmol) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) was added. The mixture was refluxed for 48 h under nitrogen atmosphere. After cooling to 0 °C, aqueous HCl (1M) was added to quench the reaction until pH = 2, and the mixture was diluted with $CHCl_3$ (150 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue dissolved in $CHCl_3$ (1.5 mL) was added dropwise into hexane (80 mL) and then the product was precipitated from the mixture. After washing with hexane, the crude product was used directly for subsequent oxidation. The crude product was dissolved in acetonitrile (20 mL), and the undissolved solid was filtered. To the solution, several drops (5 drops) of saturated solution of *p*-chloranil in acetonitrile was slowly added and stirred for 5 min. The solid precipitated immediately. Then the solid was filtered and washed with acetonitrile and acetone. The crude product was further purified by column chromatography (silica gel, $CHCl_3$) to provide the pure product **QDTP** as a brown solid in 65% yield (127 mg). Due to appearance of biradical character, the aromatic protons in ^{1}H NMR spectra changed with temperature (see Fig. 2 in main text). The purity was further confirmed by HPLC (see Fig. S12). HR-MS (MALDI-TOF, *m*/*z*): caldc for $C_{50}H_{45}N_5S_2$, 779.3111; found, 779.3128 (error = - 2.2 ppm). EA: calculated for $C_{50}H_{45}N_5S_2$, C 76.99, H 5.81, N 8.98; found: C 76.91, H 5.84, N 9.02.

For **QDTQ**, similar synthetic procedure to **QDTP** was used but further oxidation with *p*-chloranil is not necessary. The detailed procedure: after Takahashi coupling, the crude product was dissolved in $CHCl_3$ (5 mL) and the undissolved solid was filtered off. Then

the solution was concentrated into a small volume (1.5 mL) and added dropwise into hexane (80 mL). Deeply colored solid precipitated from the mixture. After filtration the crude product was washed with a large amount of hexane and acetonitrile, and finally washed with mixture of hexane and acetone (v/v = 10 :1). The crude product was further purified by flash column chromatography (silica gel, $CHCl_3$) to yield the target product **QDTQ** as a green solid in 54% yield (106 mg). No NMR spectrum for aromatic protons can be recorded at room temperature even at low temperature (-100 °C) due to the paramagnetic properties and strong aggregation. The purity was further determined by HPLC analysis with Phenomenex Li Chrosorb Diol column by using different eluents. Under variable conditions, only one elution peak was observed, indicating high purity of this compound (Fig. S13). HR-MS (MALDI-TOF, *m*/*z*): caldc for $C_{102}H_{116}N_6S_2$, 1488.8703; found, 1488.8744 (error = + 2.8 ppm). EA: calculated for $C_{102}H_{116}N_6S_2$, C 82.21, H 7.85, N 5.64; found: C 82.12, H 7.89, N 5.67.

2. UV-vis-NIR absorption spectrum of compound 7

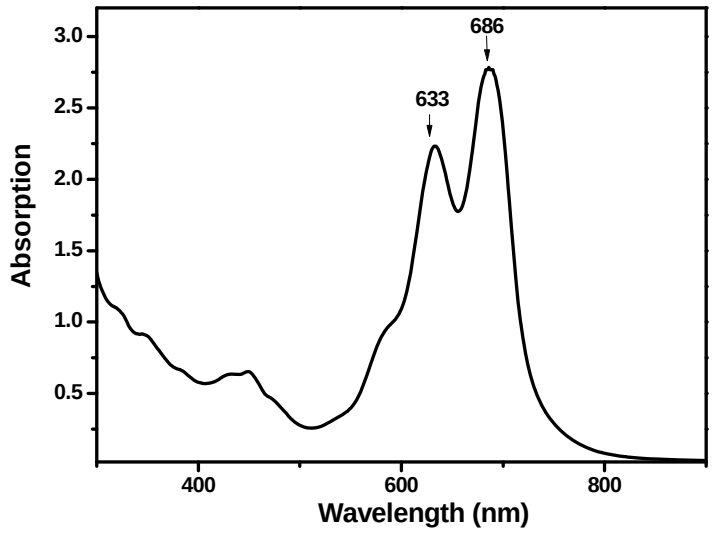


Fig. S1 UV-vis-NIR spectrum of compound **7** in DCM.

3. ESR spectra of **QDTP** and **QDTQ**

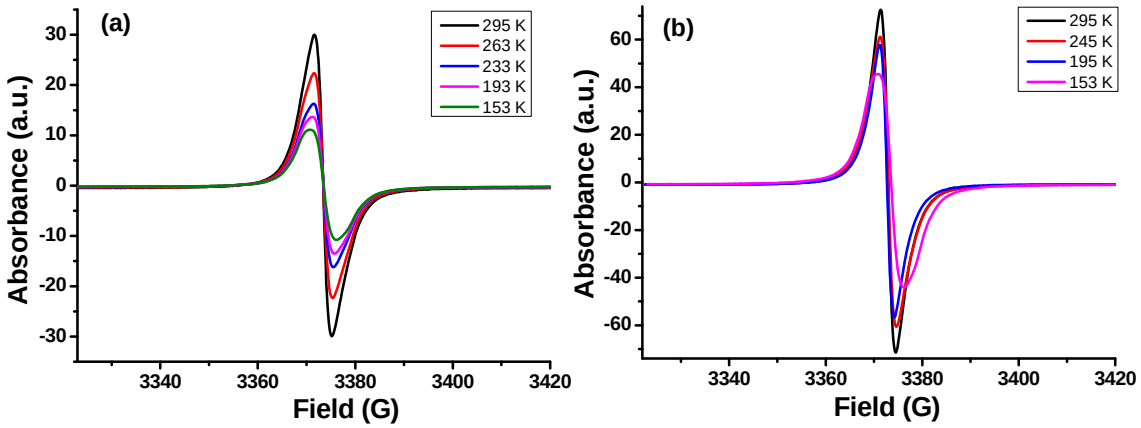


Fig. S2 VT ESR spectra of **QDTP** (a) and **QDTQ** (b) recorded in solid state.

4. Raman spectra of QDTP in solid state and in DCM

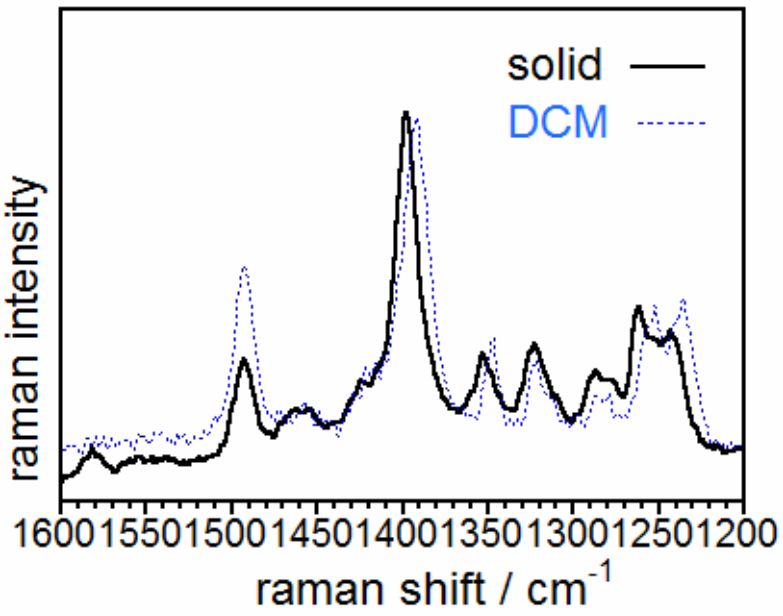


Fig. S3 The 785 nm Raman spectra of **QDTP** in solid state and in dichloromethane (DCM).

5. Femtosecond TA spectra and time decay profiles of QDTP and QDTQ

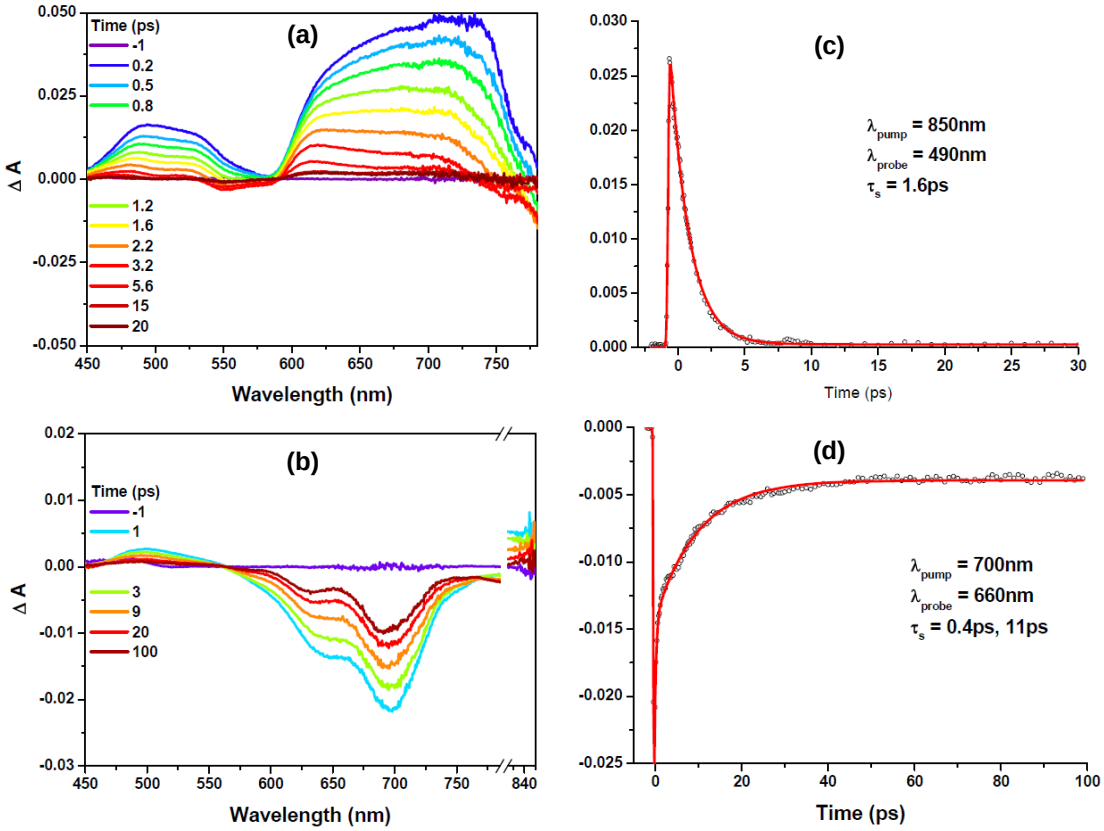


Fig. S4 Femtosecond transient absorption spectra of **QDTP** (a) and **QDTQ** (b), and the time decay profiles of **QDTP** (c) and **QDTQ** (d). All of them were recorded in DCM at room temperature.

6. Z-scan curves of QDTP and QDTQ

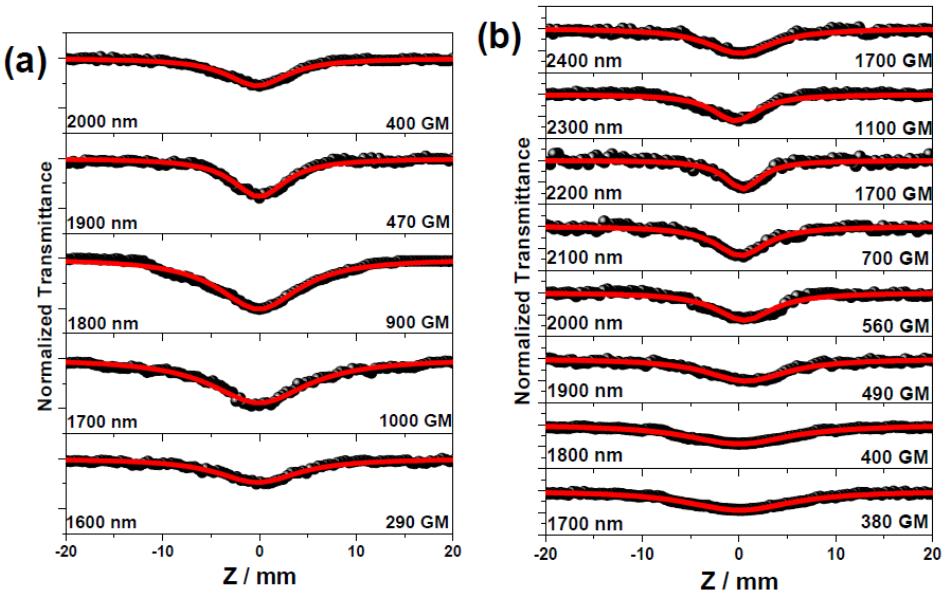


Fig. S5 Z-scan curves of (a) **QDTP** and (b) **QDTQ** by photoexcitation in the range from 1600 to 2400 nm.

7. DPV data for QDTP and QDTQ

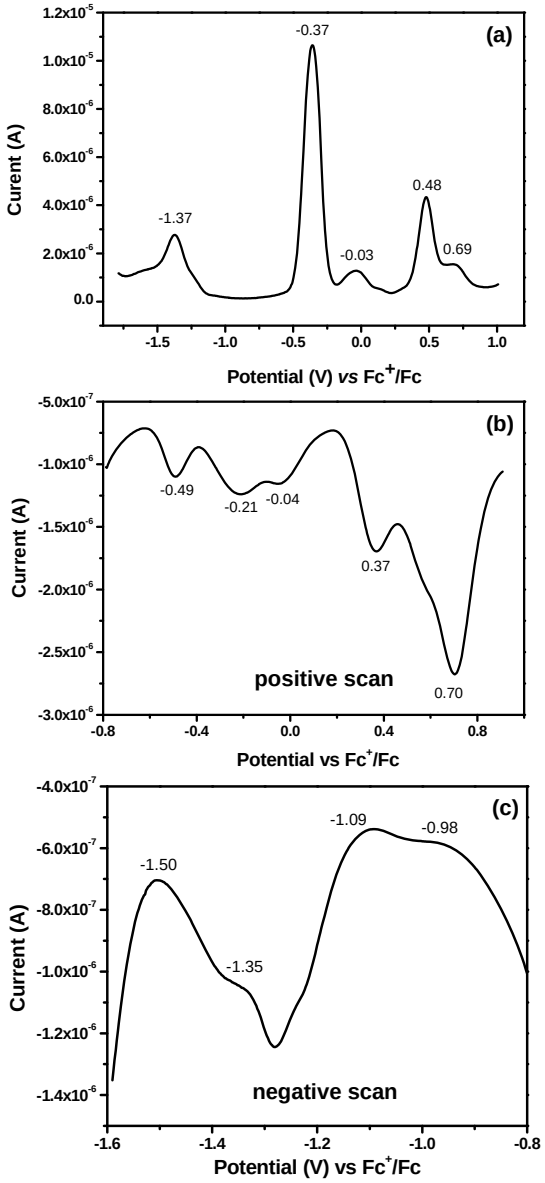


Fig. S6 Differential pulse voltammograms of **QDTP** (a) and **QDTQ** (b, c) recorded in same solution to the CV measurements.

8. DFT calculation details for QDTP and QDTQ

Theoretical calculations were performed with the *Gaussian09* program suite using a supercomputer (KISTI, IBM).[1] All calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G(d,p) basis set for all atoms.[2] To reduce the computation cost, the *N*-alkyl chains of the models of **QDTP** and **QDTQ** are replaced by methyl groups. Singlet biradical character was estimated using a CASSCF(2,2) method in the RB3LYP optimized

geometry, and using a symmetry-broken UB3LYP/6-31G** method along with geometry optimization. The biradical index *y* was determined on the basis of the LUMO occupation number. A perfect biradical is characterized by occupation numbers of 1.0 in HOMO and LUMO (i.e. y = 100%), whereas a perfect closed-shell molecule possesses occupation numbers of 2.0 and 0.0 in HOMO and LUMO (i.e. y = 0%), respectively.[3] The global ring centers for the NICS(1) values were designated at the non-weighted mean centers of the rings. The $NICS(1)_{zz}$ means total MO contribution to the zz component of the NICS tensor.[4] The NICS value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries. To simulate the ground-state absorption spectra, the time-dependent (TD) DFT calculation was employed with UB3LYP/6-31G(d,p) level. The energies and Cartesian coordinates for all optimized structures are attached as appendix at the end of this supporting information.

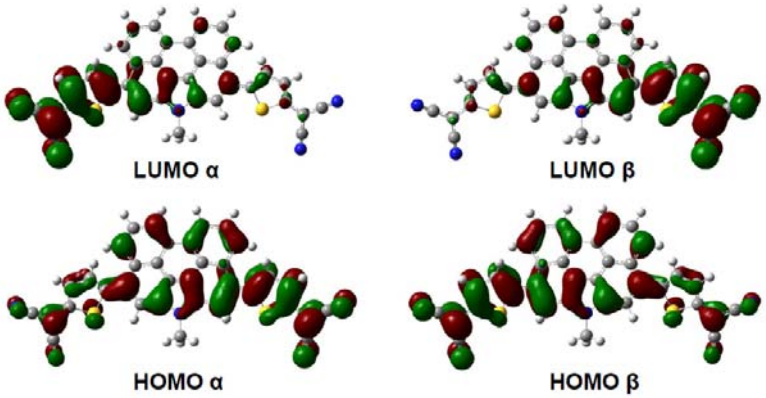


Fig. S7 DFT (BS-UB3LYP) calculated frontier molecular orbitals of **QDTP** (singlet biradical (SB), *N*-substituent is methyl group).

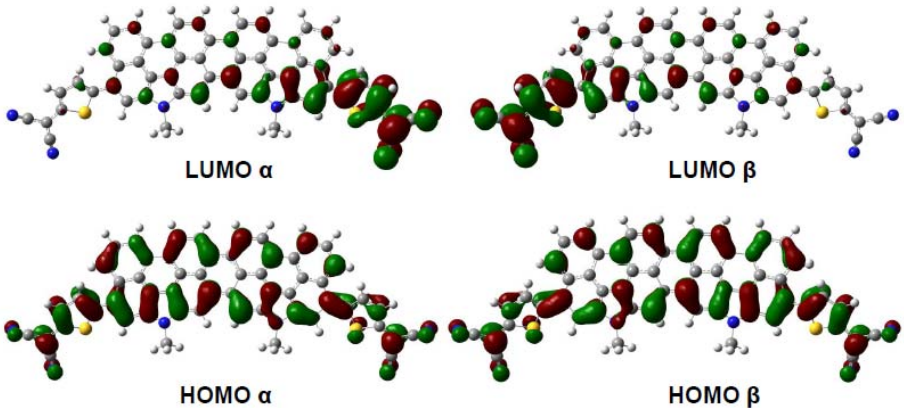


Fig. S8 DFT (BS-UB3LYP) calculated frontier molecular orbitals of **QDTQ** (SB, *N*-substituent is methyl group).

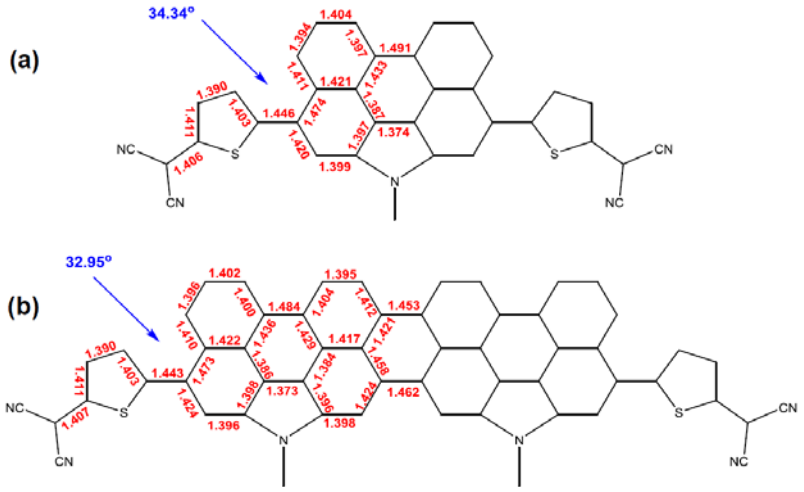


Fig. S9 DFT calculated optimized geometric structure of (a) **QDTP** and (b) **QDTQ**, their bond lengths (with part of the bonds labeled with length in Å), and the dihedral angle (with angle labelled in °) between rylene core and thiophene moiety of the singlet biradical (SB) form.

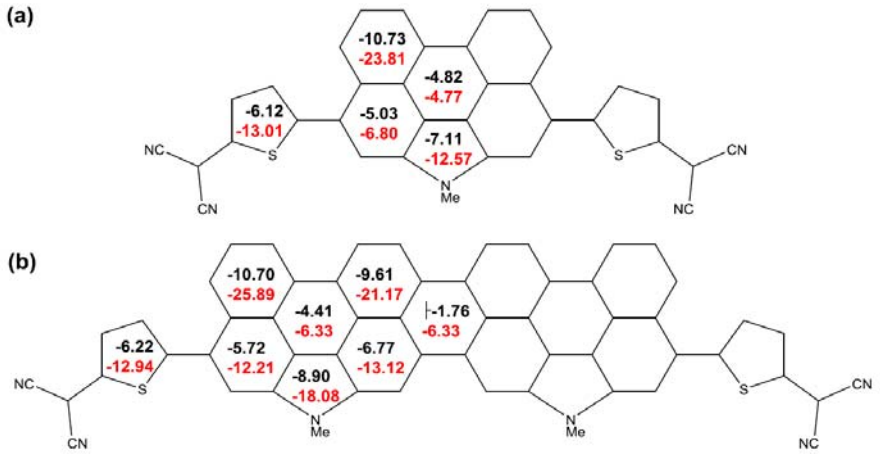


Fig. S10 Calculated NICS(1) and NICS(1)$_{zz}$ values for a) **QDTP** (SB) and **QDTQ** (SB) (BS-UB3LYP). NICS(1): black color; NICS(1)zz: red color.

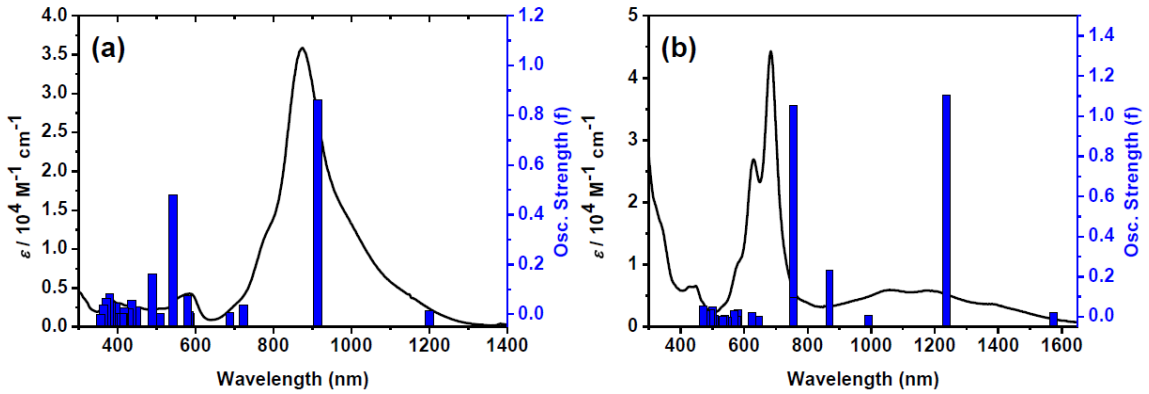


Fig. S11 TD DFT simulated spectrum of **QDTP** (a) and **QDTQ** (b) along with experimental spectrum.

Table S1. Selected TD-DFT (UB3LYP/6-31G(d,p)) calculated energies, oscillator strength and compositions of major electronic transitions of **QDTP**. The α and β-orbitals are distinguished as A and B in the parenthesis, respectively.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
1199.99358	0.0137	HOMO(A)->LUMO(A) (48%), HOMO(B)->LUMO(B) (48%)
913.72494	0.8607	HOMO(A)->LUMO(A) (43%), HOMO(B)->LUMO(B) (43%)
722.05076	0.0374	H-1(A)->LUMO(A) (41%), H-1(B)->LUMO(B) (41%)
580.14757	0.075	H-2(A)->LUMO(A) (12%), H-1(A)->LUMO(A) (17%)
489.64629	0.1621	H-3(A)->LUMO(A) (37%), H-3(B)->LUMO(B) (37%)

Table S2. Selected TD-DFT (UB3LYP/6-31G(d,p)) calculated energies, oscillator strength and compositions of major electronic transitions of **QDTQ**. The α and β-orbitals are distinguished as A and B in the parenthesis, respectively.

Wavelength (nm)	Osc. Strength (f)	Major Contributions
1573.79204	0.0199	HOMO(A)->LUMO(A) (45%), HOMO(B)->LUMO(B) (45%)
1237.35865	1.1065	HOMO(A)->LUMO(A) (42%), HOMO(B)->LUMO(B) (42%)
869.02178	0.2326	H-1(A)->LUMO(A) (39%), H-1(B)->LUMO(B) (39%)
755.39716	1.0525	HOMO(A)->L+1(A) (42%), HOMO(B)->L+1(B) (43%)
754.9372	0.096	H-1(A)->LUMO(A) (40%), H-1(B)->LUMO(B) (40%)
500.27574	0.0471	H-5(A)->LUMO(A) (27%), H-2(A)->LUMO(A) (11%), H-5(B)->LUMO(B) (27%), H-2(B)->LUMO(B) (11%)
1573.79204	0.0199	HOMO(A)->LUMO(A) (45%), HOMO(B)->LUMO(B) (45%)

References:

(1) Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

(2) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(3) Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 170.189.

(4) H. Fallah-Bagher-Shaidaei, S. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863.

9. ^{1}H, ^{13}C NMR spectra, mass spectra and HPLC curves

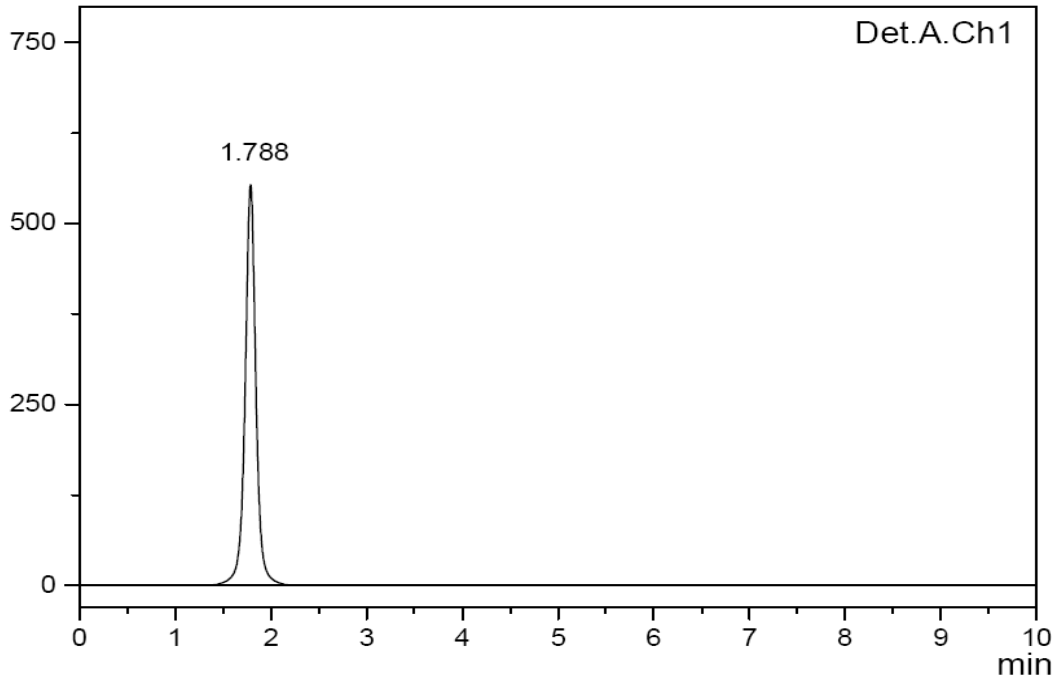


Fig. S12 Representative HPLC curve of compound **QDTP**. Phenomenex Li Chrosorb Diol column (250mm × 3.2 mm), hexane/THF = 50/50 as eluent, flow rate 1 mL min^{-1}, and detection wavelength is 584 nm.

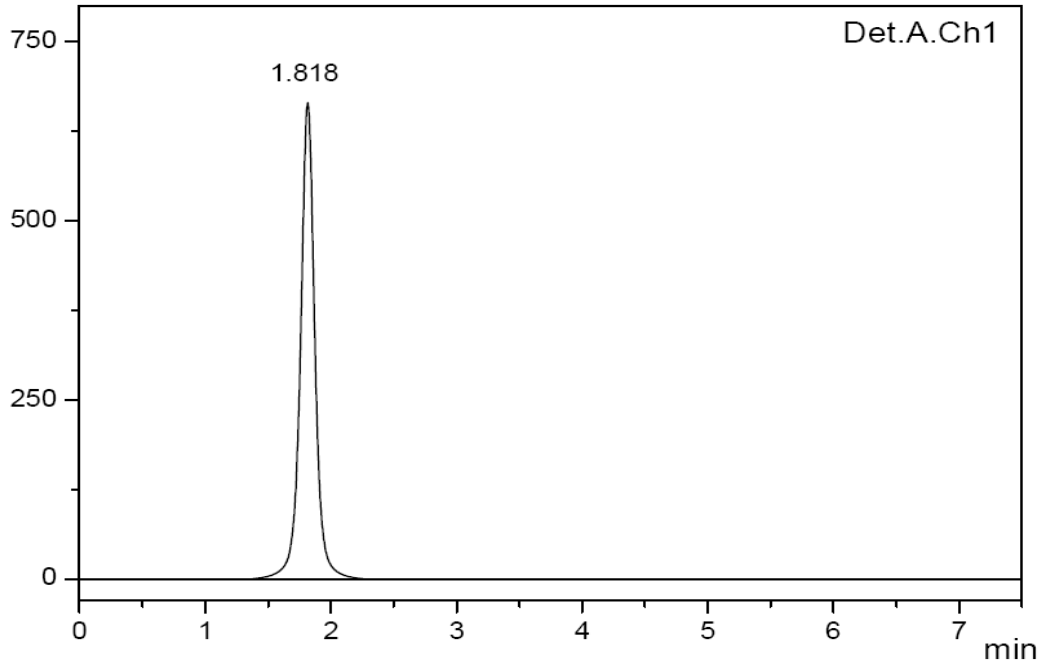


Fig. S13 Representative HPLC curve of compound **QDTQ**. Phenomenex Li Chrosorb Diol column (250mm × 3.2 mm), hexane/THF = 50/60 as eluent, flow rate 1 mL min^{-1}, and detection wavelength is 685 nm.

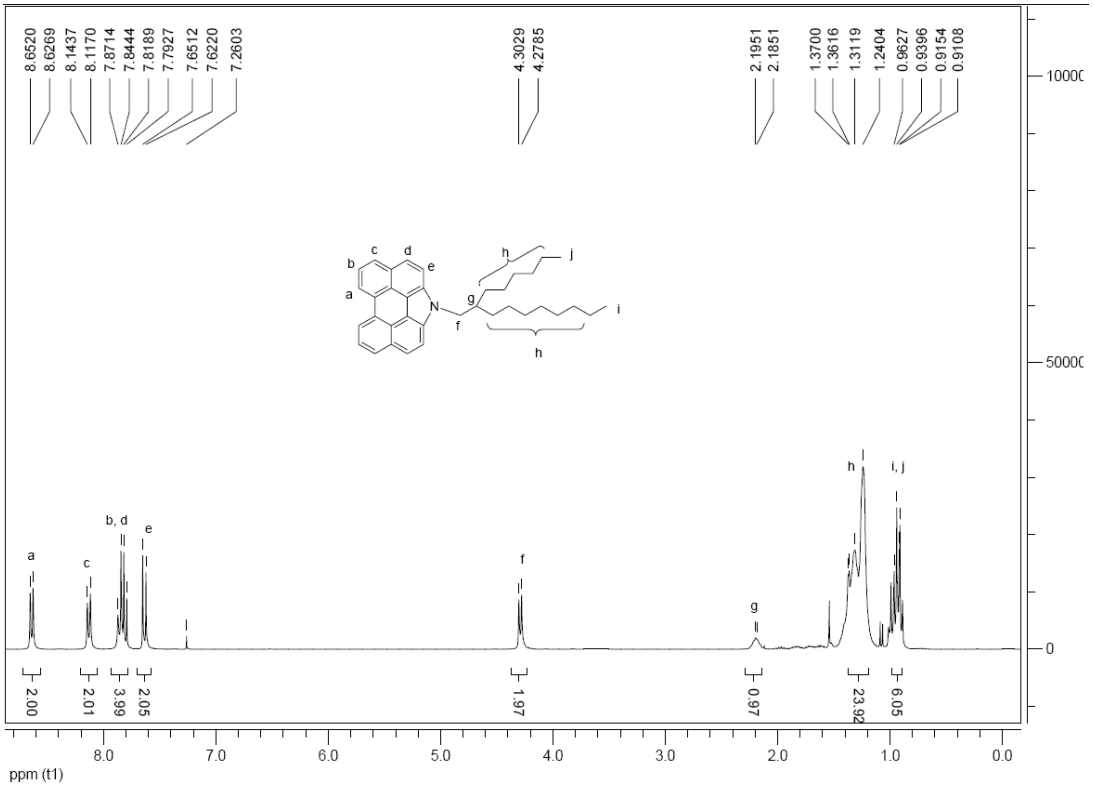


Fig. S14 ^{1}H NMR spectrum (300 MHz) of compound **9** in $CDCl_3$ at 298 K.

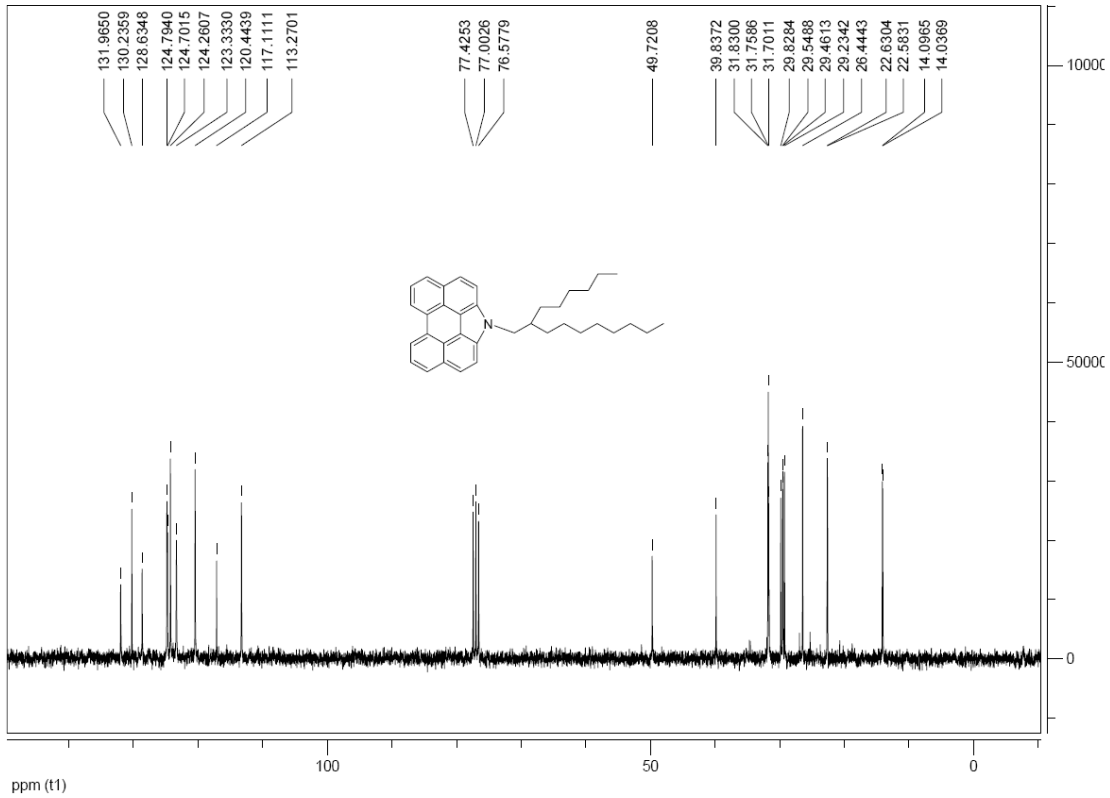


Fig. S15 ^{13}C NMR spectrum (75 MHz) of compound **9** in $CDCl_3$ at 298 K.

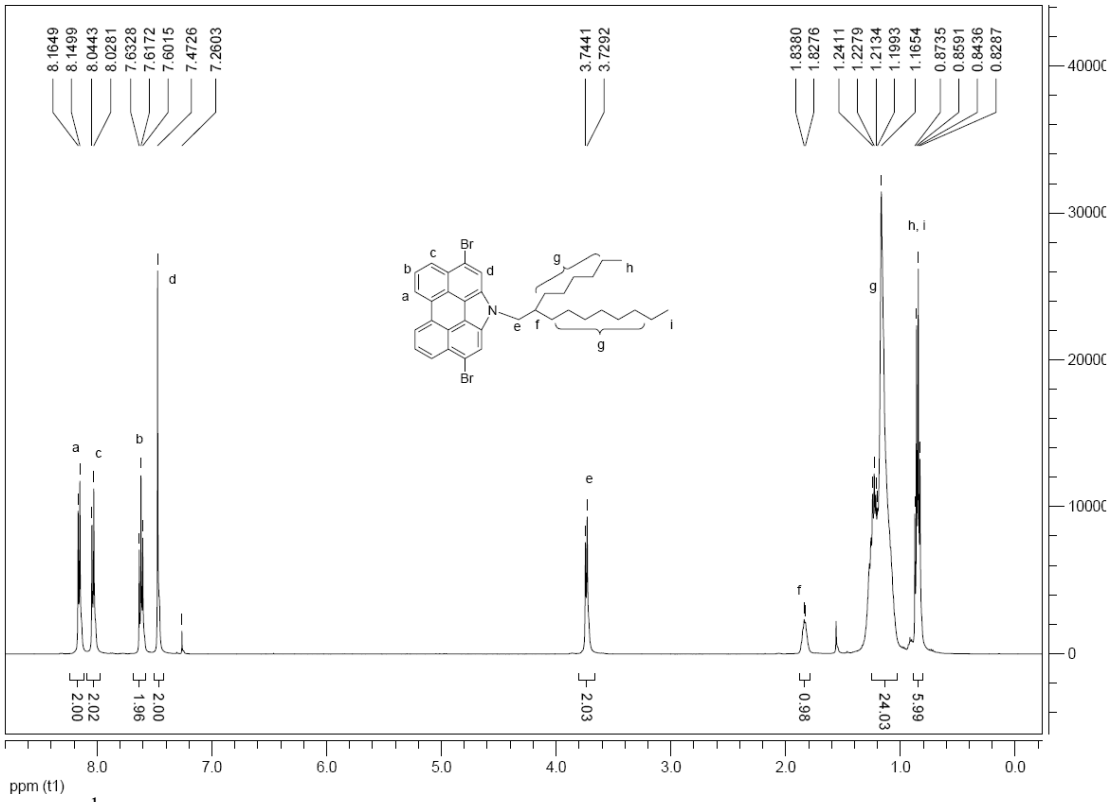


Fig. S16 ^{1}H NMR spectrum (500 MHz) of compound **1** in $CDCl_3$ at 298 K.

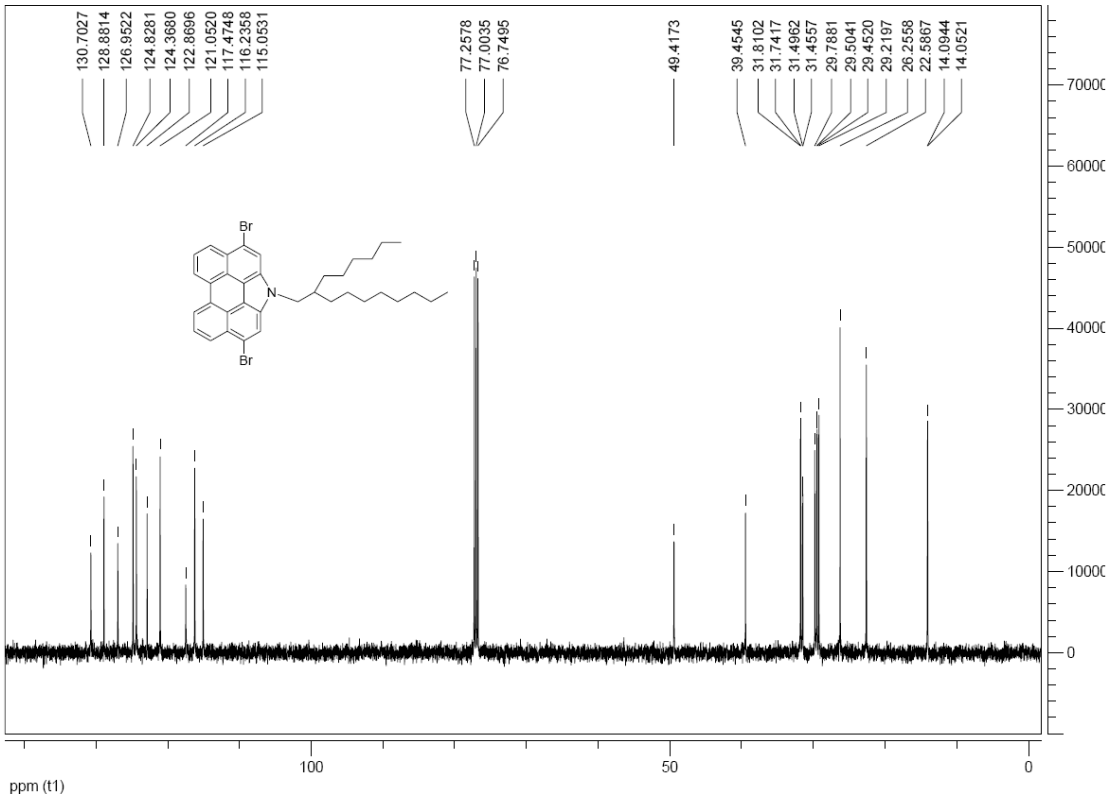


Fig. S17 ^{13}C NMR spectrum (125 MHz) of compound **1** in $CDCl_3$ at 298 K.

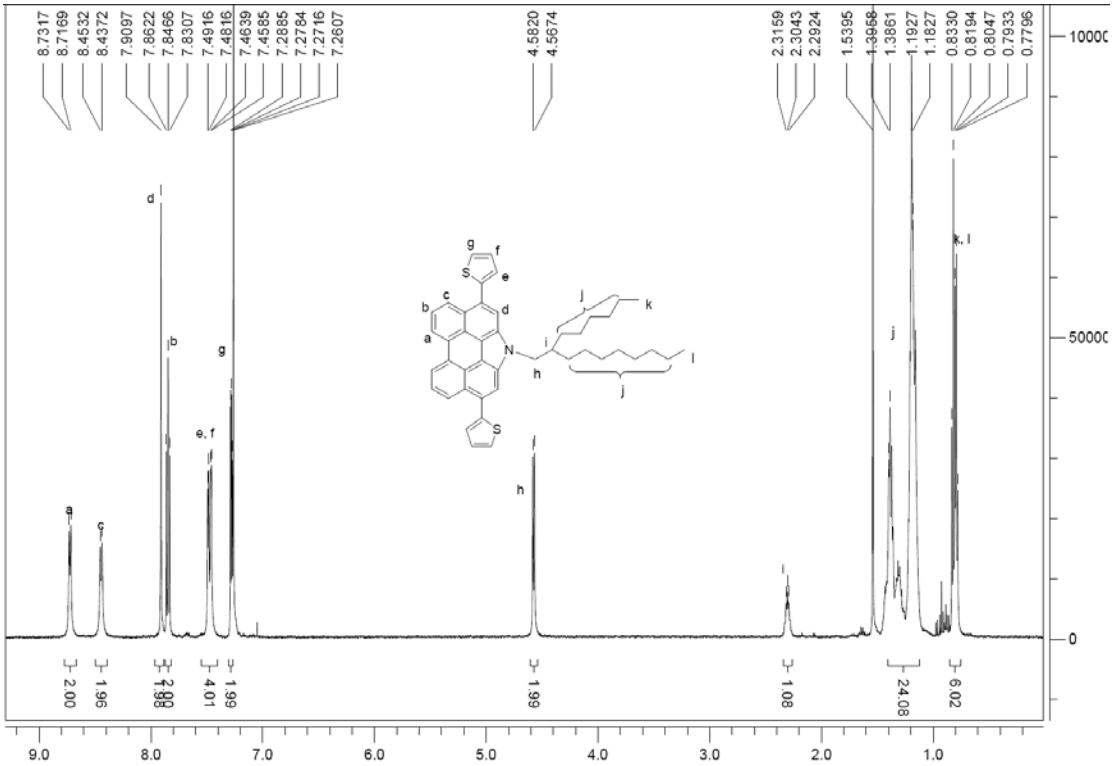


Fig. S18 ^{1}H NMR spectrum (500 MHz) of compound **2** in $CDCl_3$ at 298 K.

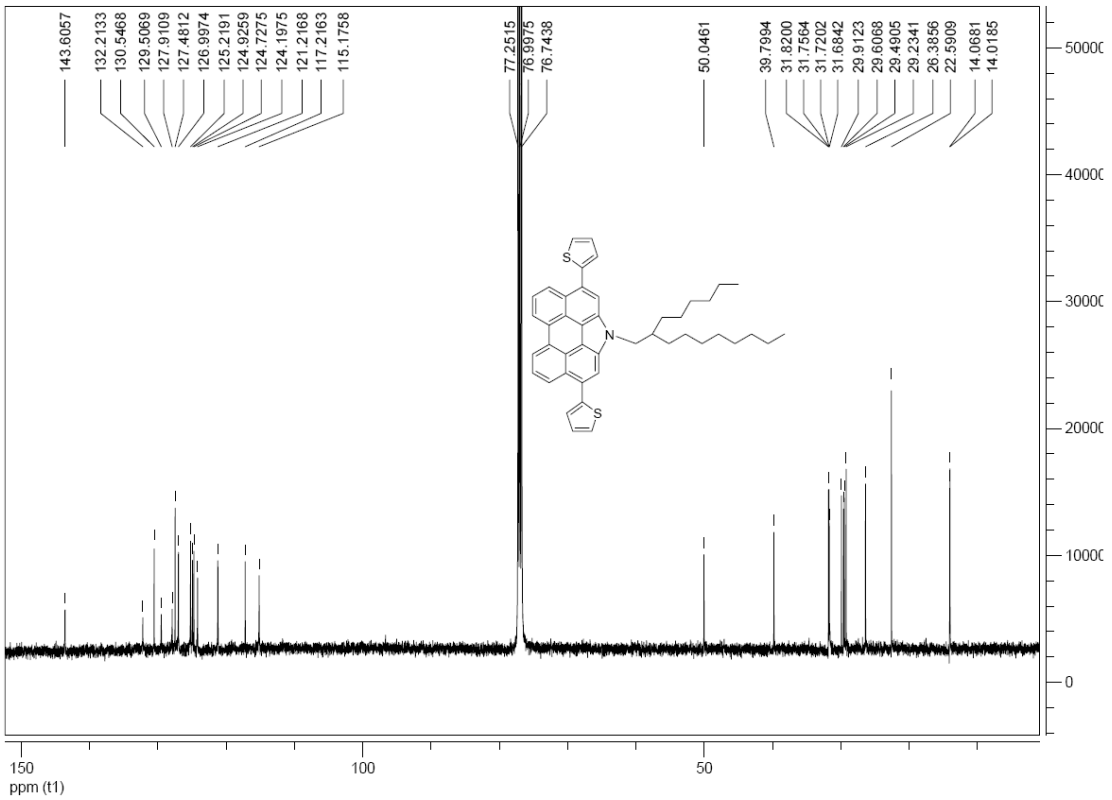


Fig. S19 ^{13}C NMR spectrum (125 MHz) of compound **2** in $CDCl_3$ at 298 K.

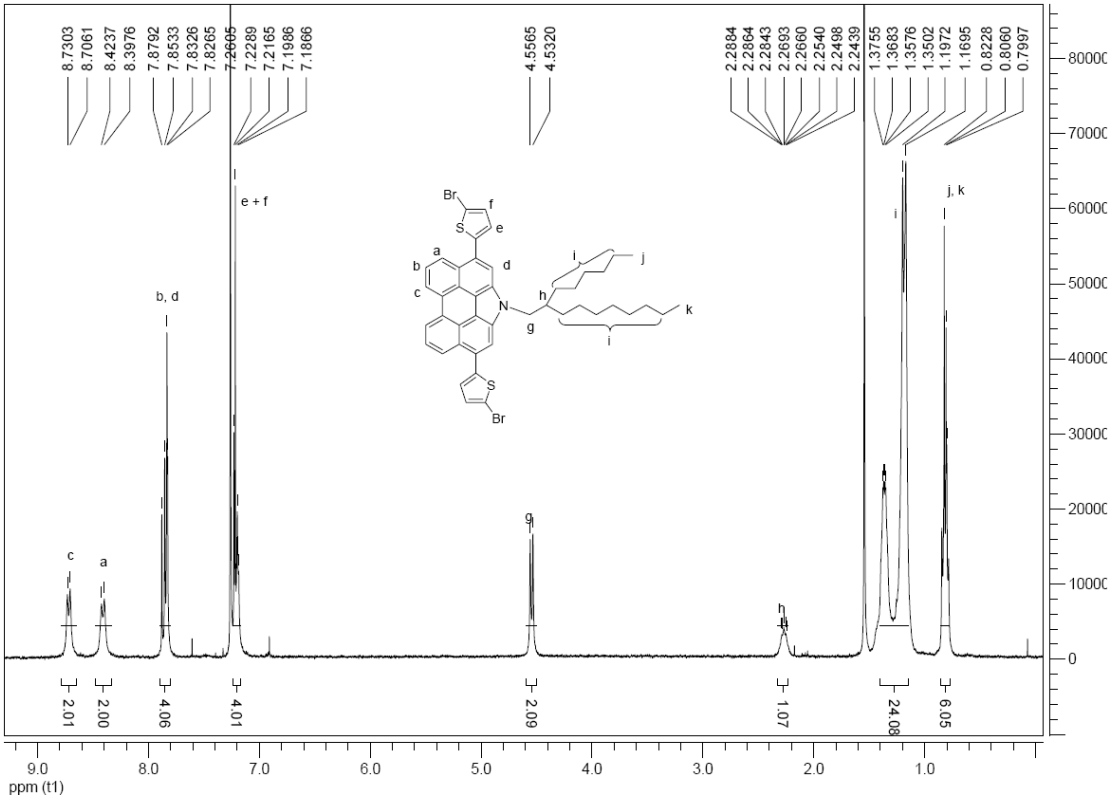


Fig. S20 ^{1}H NMR spectrum (300 MHz) of compound **3** in $CDCl_3$ at 298 K.

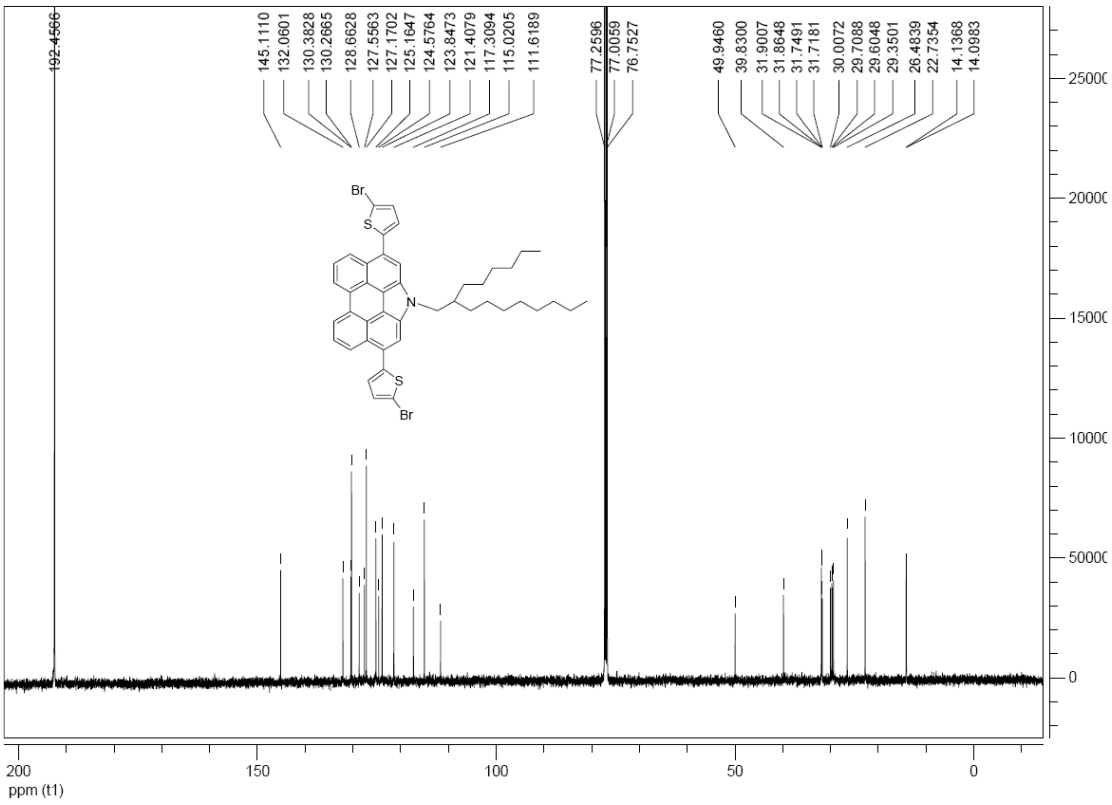


Fig. S21 ^{13}C NMR spectrum (75 MHz) of compound **3** in $CDCl_3$ at 298 K.

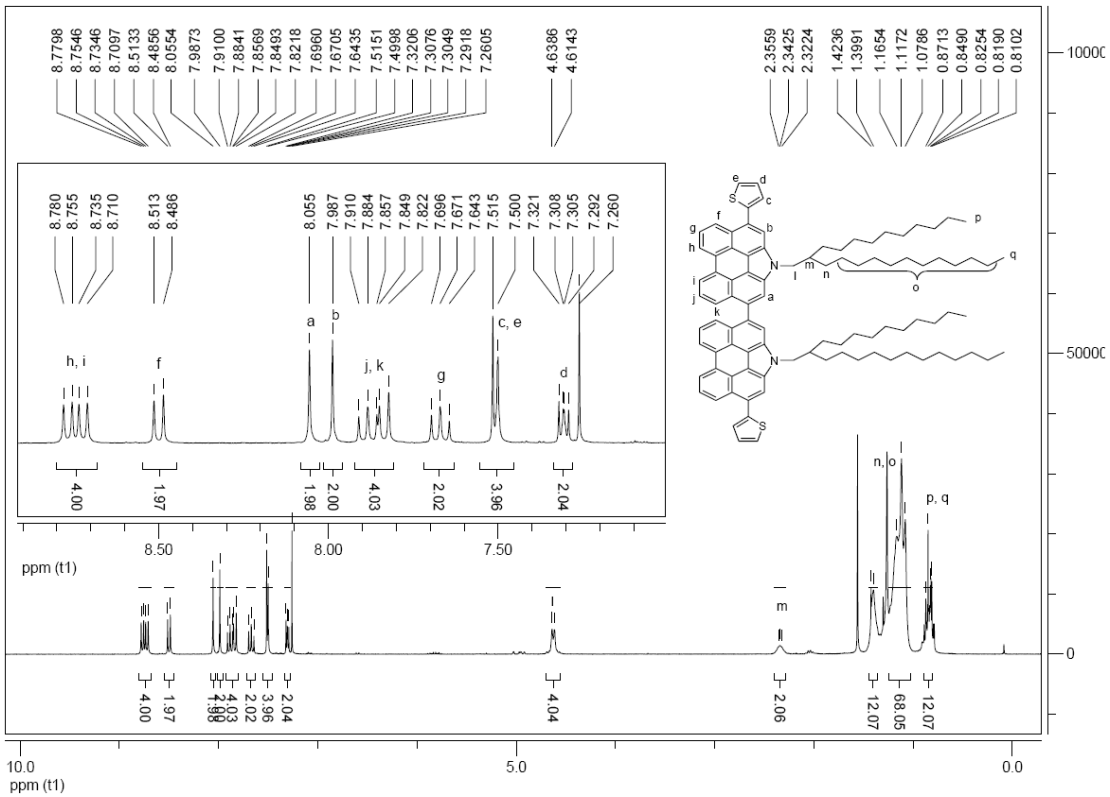


Fig. S22 ^{1}H NMR spectrum (300 MHz) of compound **5** in $CDCl_3$ at 298 K.

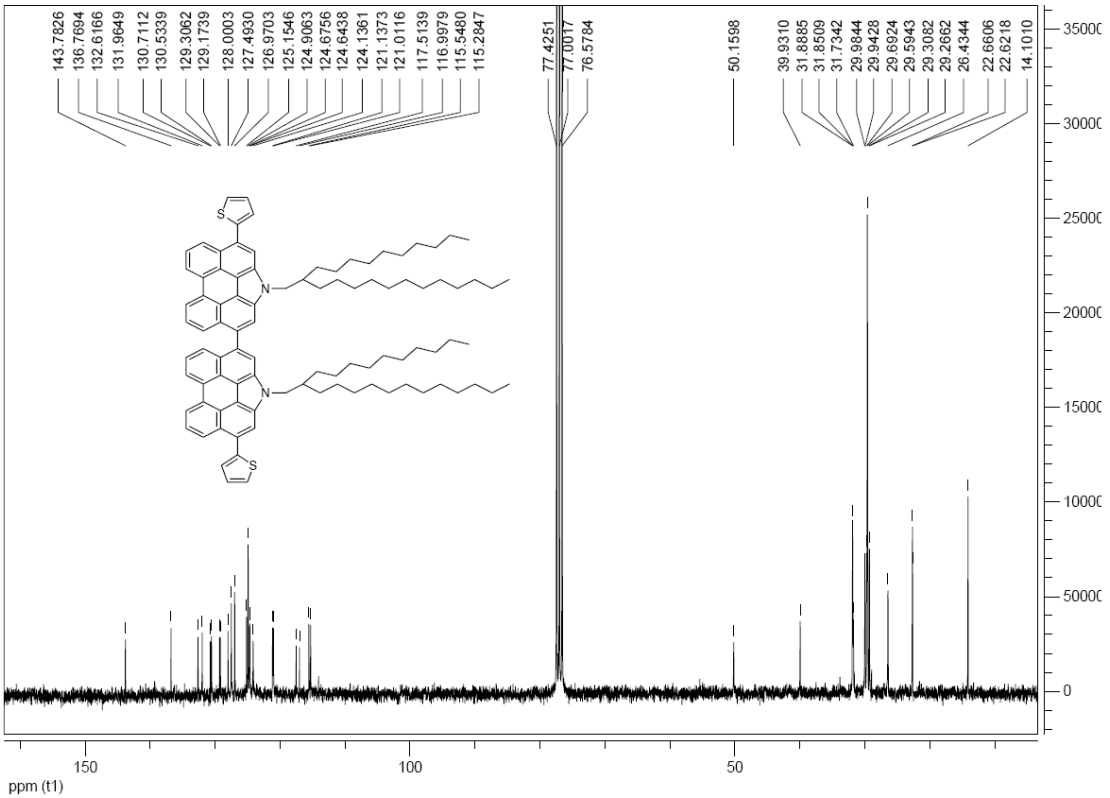


Fig. S23 ^{13}C NMR spectrum (75 MHz) of compound **5** in $CDCl_3$ at 298 K.

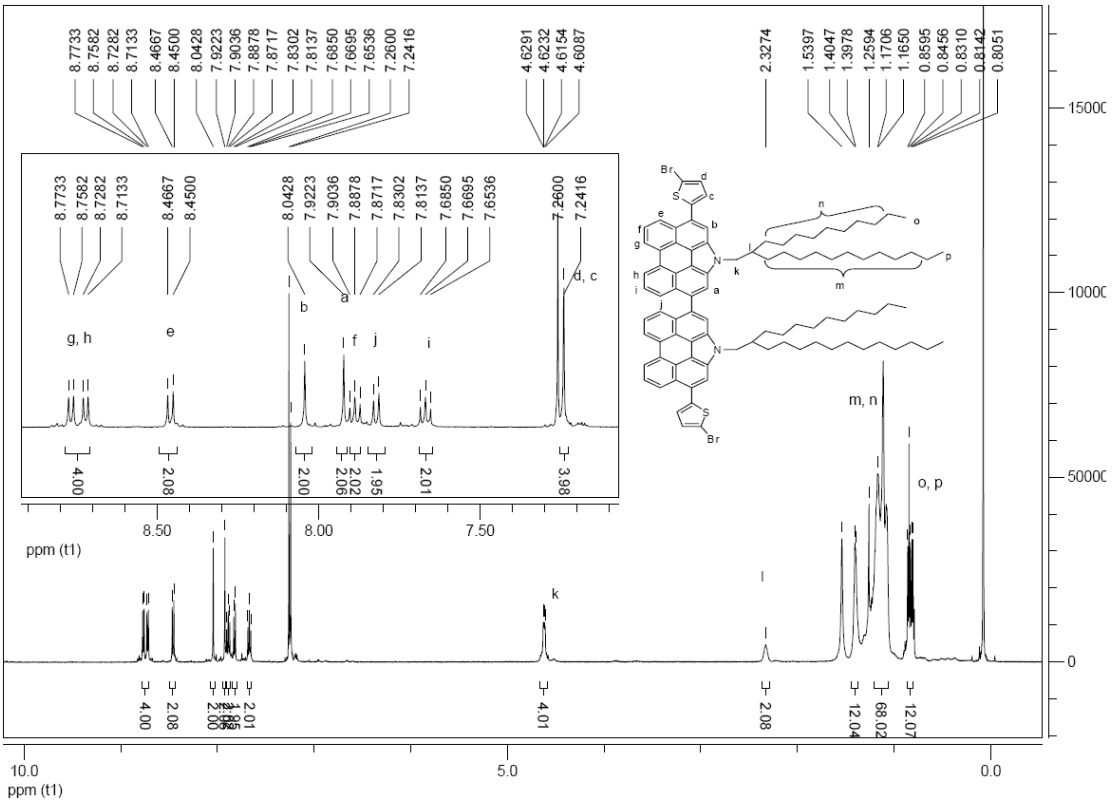


Fig. S24 ^{1}H NMR spectrum (500 MHz) of compound **6** in $CDCl_3$ at 298 K.

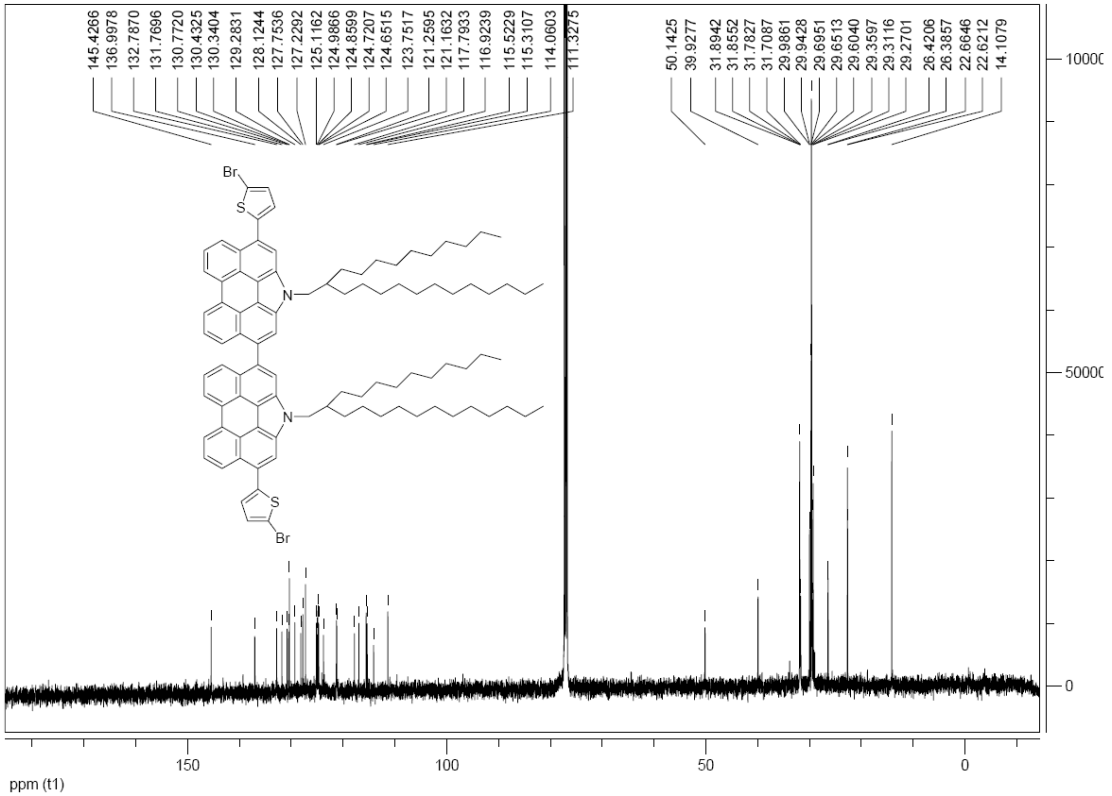


Fig. S25 ^{13}C NMR spectrum (125 MHz) of compound **6** in $CDCl_3$ at 298 K.

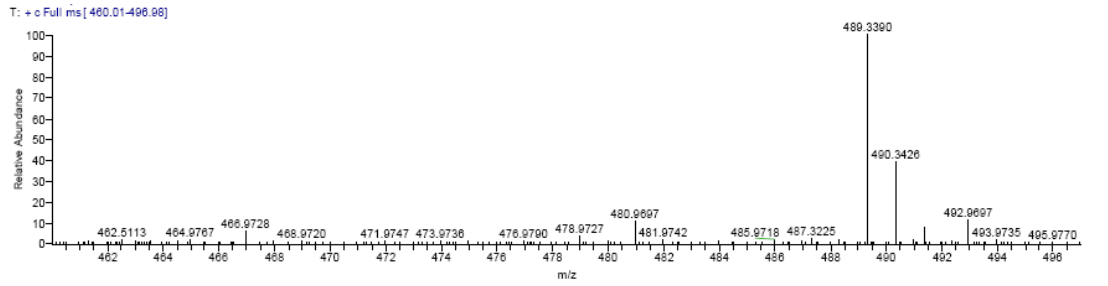


Fig. S26 HR mass spectrum (EI) of compound **9**.

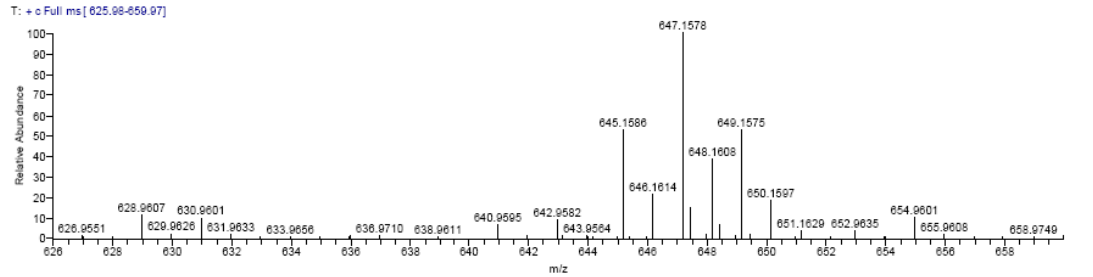


Fig. S27 HR mass spectrum (EI) of compound **1**.

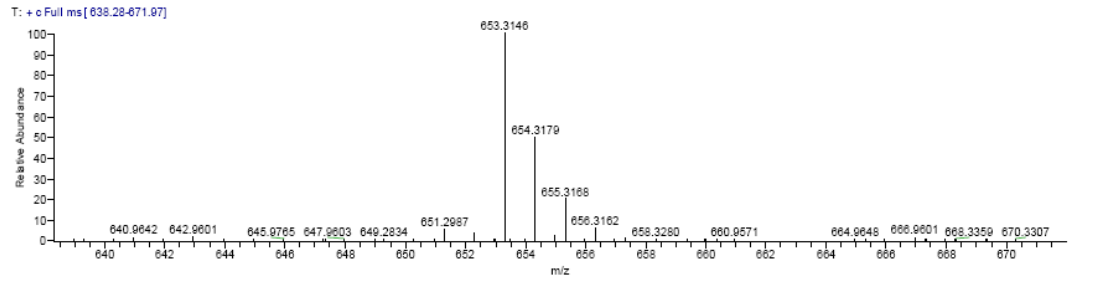


Fig. S28 HR mass spectrum (EI) of compound **2**.

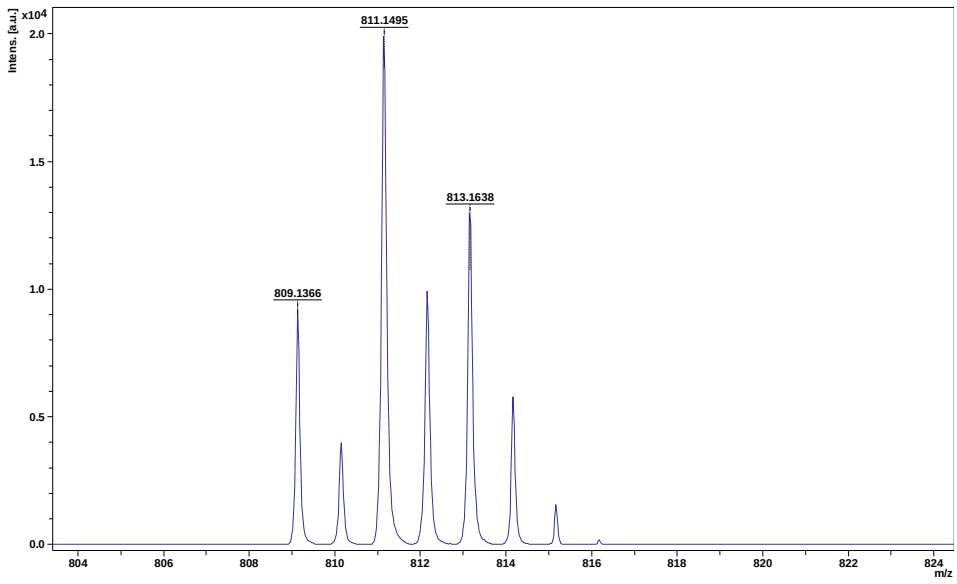


Fig. S29 HR mass spectrum (MALDI-TOF) of compound **3**.

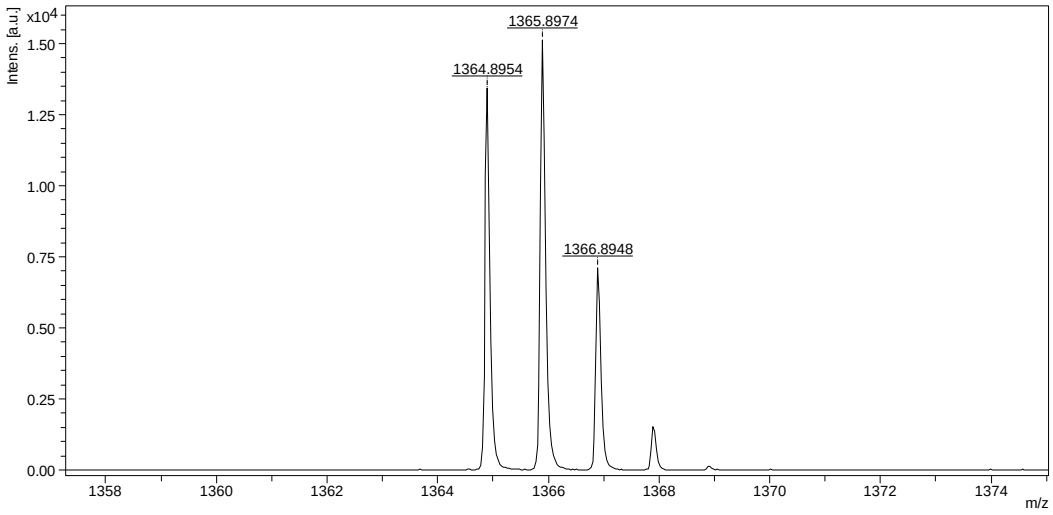


Fig. S30 HR mass spectrum (MALDI-TOF) of compound **5**.

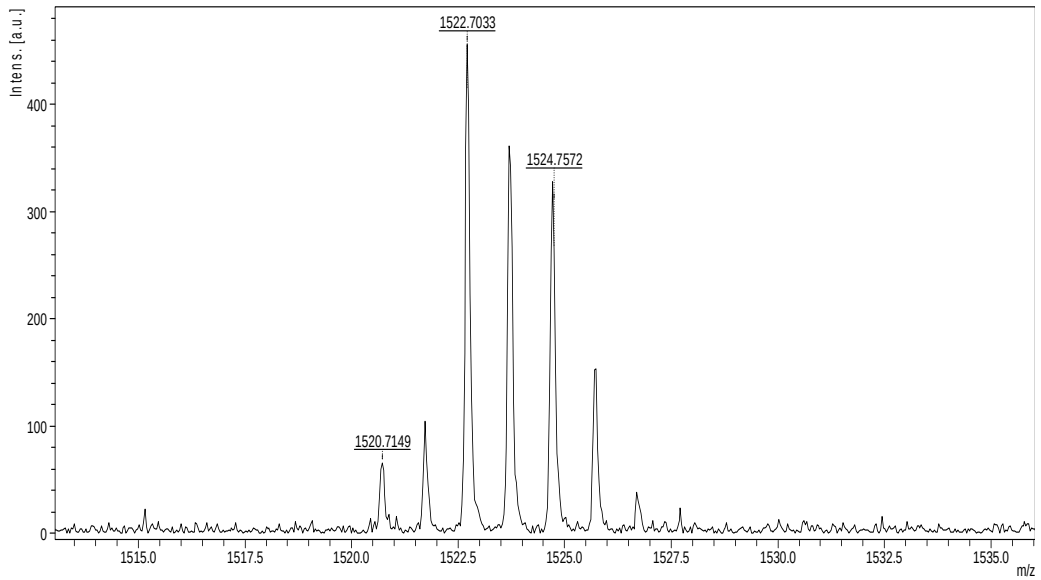


Fig. S31 HR mass spectrum (MALDI-TOF) of compound **6**.

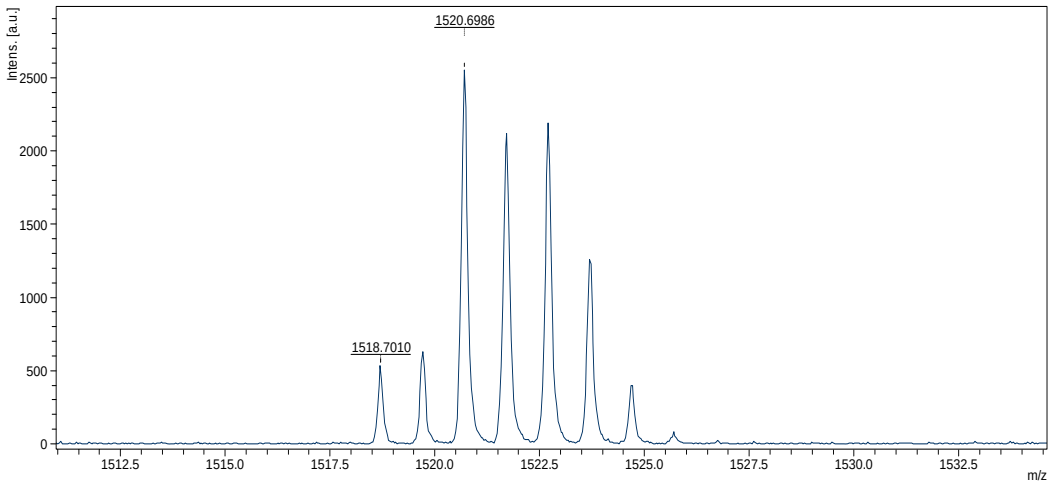


Fig. S32 HR mass spectrum (MALDI-TOF) of compound **7**.

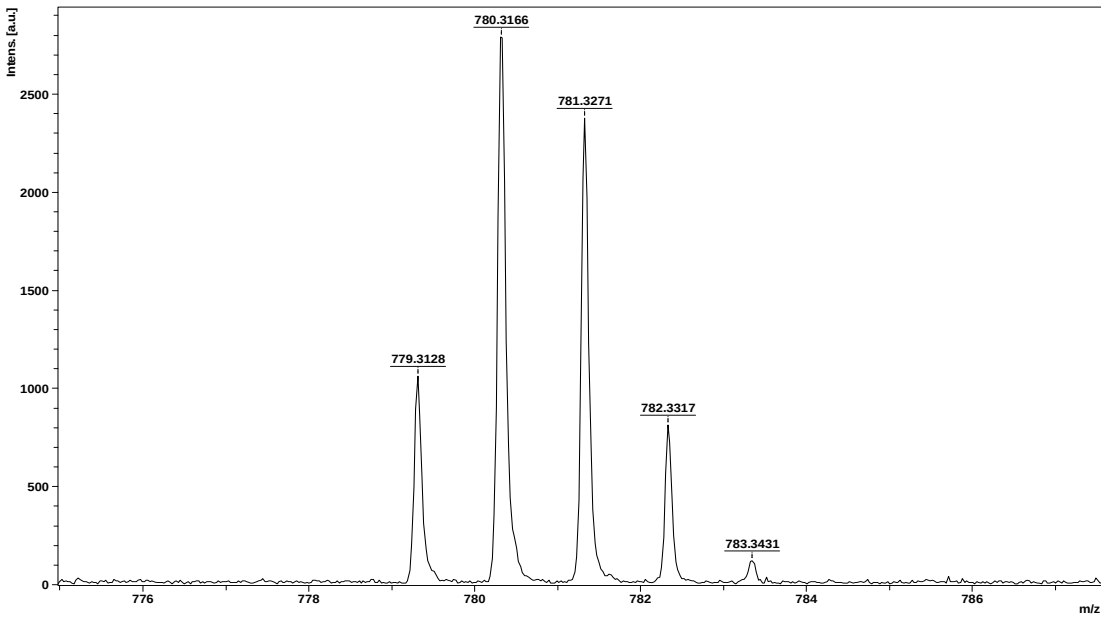


Fig. S33 HR mass spectrum (MALDI-TOF) of compound **QDTP**.

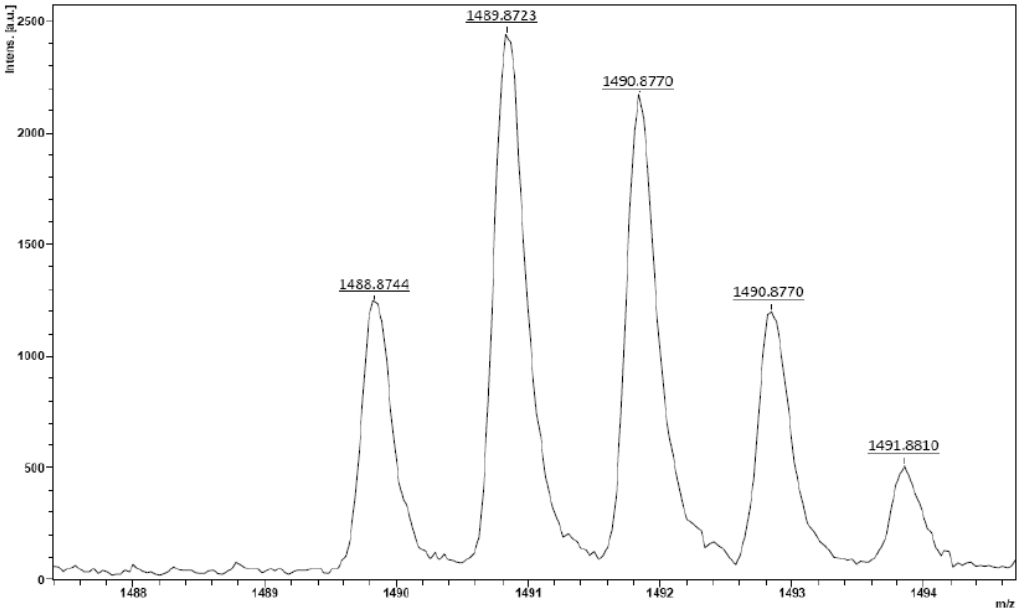


Fig. S34 HR mass spectrum (MALDI-TOF) of compound **QDTQ**.

10. Appendix: energies and Cartesian coordinates of all optimized structures

QDTP in the singlet state (CS; rb3lyp/6-31g(d,p))

Total Energy (Hartree):

Row	Symbol	X	Y	Z
1	C	2.9356960	4.1058280	-0.3562070
2	H	4.6575720	2.8431780	-0.4987880
3	C	3.5892110	2.8664960	-0.3277450
4	C	0.7420200	3.0885720	-0.1410080
5	C	2.8567670	1.6831600	-0.1404100
6	C	1.5491540	4.2324430	-0.2499990
7	C	1.4461560	1.8445780	-0.0896800
8	C	3.3923780	0.2944960	-0.0907260
9	H	1.1079790	5.2228400	-0.2917100
10	C	2.5072910	-0.8454880	-0.1953020
11	H	2.9396170	-1.8395420	-0.2016590
12	C	1.1430590	-0.6496520	-0.1783700
13	C	0.6795580	0.6830170	-0.0845070
14	C	-1.1430550	-0.6496590	-0.1783730
15	C	-0.6795600	0.6830130	-0.0845090
16	C	-3.3923770	0.2944880	-0.0907330
17	C	-1.4461600	1.8445730	-0.0896810
18	C	-2.5072880	-0.8454940	-0.1953090
19	C	-2.8567710	1.6831520	-0.1404120
20	C	-0.7420280	3.0885690	-0.1410070
21	H	-2.9396160	-1.8395460	-0.2016700
22	H	-4.6575810	2.8431640	-0.4987770
23	C	-1.5491660	4.2324380	-0.2499950
24	H	-1.1079940	5.2228360	-0.2917040
25	C	-2.9357080	4.1058200	-0.3562000
26	H	-3.5330460	5.0021780	-0.4916280
27	C	-3.5892190	2.8664860	-0.3277400
28	N	0.0000060	-1.4690570	-0.2085070
29	C	0.0000370	-2.9152960	-0.3491150
30	H	-0.8835930	-3.3290040	0.1415440
31	H	0.8832480	-3.3290590	0.1422620
32	C	4.7698520	0.0469170	0.0874010
33	C	-4.7698520	0.0469100	0.0873910
34	C	5.7672000	0.8723020	0.6768620
35	H	5.5385210	1.8476660	1.0838000
36	C	7.0093320	0.2968370	0.7859770
37	H	7.8707580	0.7700050	1.2411540
38	C	7.0713330	-1.0322340	0.2753350
39	C	8.1859170	-1.8667690	0.2351950
40	C	-5.7671990	0.8723030	0.6768410

41	H	-5.5385190	1.8476720	1.0837680
42	C	-7.0093320	0.2968400	0.7859610
43	H	-7.8707580	0.7700140	1.2411330
44	C	-7.0713330	-1.0322360	0.2753320
45	C	-8.1859180	-1.8667710	0.2352010
46	S	5.4960320	-1.5239040	-0.3304120
47	S	-5.4960340	-1.5239130	-0.3304120
48	C	9.4433800	-1.3952400	0.7045130
49	C	8.1003230	-3.1936560	-0.2659760
50	C	-8.1003250	-3.1936630	-0.2659580
51	C	-9.4433810	-1.3952370	0.7045140
52	N	10.4605560	-0.9826730	1.0980320
53	N	7.9952630	-4.2780970	-0.6824620
54	N	-7.9952660	-4.2781080	-0.6824350
55	N	-10.4605590	-0.9826640	1.0980240
56	H	3.5330310	5.0021870	-0.4916400
57	H	0.0004510	-3.2224090	-1.4008330

QDTP in the singlet biradical state (SB; BS-ub3lyp/6-31G(d,p))

Total Energy (Hartree): -2412.8363

<S2>: 0.9427

Row	Symbol	X	Y	Z
1	C	2.9511620	4.0394980	-0.4669550
2	H	4.6819240	2.7837340	-0.4378140
3	C	3.6050600	2.8156460	-0.3298070
4	C	0.7456450	3.0413320	-0.2426170
5	C	2.8615980	1.6384570	-0.1004070
6	C	1.5539000	4.1686280	-0.4137260
7	C	1.4491650	1.8009740	-0.0940410
8	C	3.3848420	0.2695580	0.0599430
9	H	1.1162750	5.1543380	-0.5348690
10	C	2.5272010	-0.8614710	0.1197340
11	H	2.9686650	-1.8444380	0.2437400
12	C	1.1403640	-0.6733730	0.0961190
13	C	0.6874660	0.6456520	0.0124170
14	C	-1.1403840	-0.6733560	0.0961500
15	C	-0.6874680	0.6456680	0.0124380
16	C	-3.3848450	0.2696020	0.0600180
17	C	-1.4491530	1.8009970	-0.0940010
18	C	-2.5272200	-0.8614380	0.1198000
19	C	-2.8615930	1.6384910	-0.1003310
20	C	-0.7456280	3.0413460	-0.2425900
21	H	-2.9687090	-1.8443910	0.2438210
22	H	-4.6819130	2.7838020	-0.4376580

23	C	-1.5538710	4.1686570	-0.4136620
24	H	-1.1162320	5.1543610	-0.5347900
25	C	-2.9511350	4.0395440	-0.4668430
26	H	-3.5478310	4.9300530	-0.6396530
27	C	-3.6050440	2.8156970	-0.3296890
28	N	-0.0000100	-1.4927550	0.1683860
29	C	0.0000070	-2.9454480	0.2045190
30	H	-0.8838090	-3.2972000	0.7409870
31	H	0.8832040	-3.2971910	0.7420250
32	C	4.8066950	0.0389600	0.1870480
33	C	-4.8067070	0.0390160	0.1871120
34	C	5.7814830	0.8343400	0.8074190
35	H	5.5405070	1.7732820	1.2883090
36	C	7.0536900	0.2736540	0.8303340
37	H	7.9197040	0.7318410	1.2926720
38	C	7.1202860	-0.9937870	0.2130450
39	C	8.2542900	-1.8128350	0.0662580
40	C	-5.7815270	0.8343410	0.8074650
41	H	-5.5406110	1.7732890	1.2883780
42	C	-7.0537270	0.2736270	0.8303400
43	H	-7.9197580	0.7317980	1.2926620
44	C	-7.1202800	-0.9938090	0.2130320
45	C	-8.2542800	-1.8128570	0.0662350
46	S	5.5385810	-1.4569050	-0.3994370
47	S	-5.5385650	-1.4568720	-0.3994540
48	C	9.5160850	-1.3678870	0.5424810
49	C	8.1747670	-3.0884110	-0.5490030
50	C	-8.1747620	-3.0884150	-0.5490650
51	C	-9.5160790	-1.3679270	0.5424660
52	N	10.5395020	-0.9780950	0.9446760
53	N	8.0788530	-4.1341280	-1.0583320
54	N	-8.0788560	-4.1341100	-1.0584410
55	N	-10.5395070	-0.9781390	0.9446350
56	H	3.5478540	4.9300020	-0.6398020
57	H	0.0005930	-3.3782940	-0.8020430

QDTP in the triplet state (TB; ub3lyp/6-31g(d,p))

Total Energy (Hartree): -2412.8337

<S2>: 2.0464

Row	Symbol	X	Y	Z
1	C	2.9511620	4.0394980	-0.4669550
2	H	4.6819240	2.7837340	-0.4378140
3	C	3.6050600	2.8156460	-0.3298070
4	C	0.7456450	3.0413320	-0.2426170

5	C	2.8615980	1.6384570	-0.1004070
6	C	1.5539000	4.1686280	-0.4137260
7	C	1.4491650	1.8009740	-0.0940410
8	C	3.3848420	0.2695580	0.0599430
9	H	1.1162750	5.1543380	-0.5348690
10	C	2.5272010	-0.8614710	0.1197340
11	H	2.9686650	-1.8444380	0.2437400
12	C	1.1403640	-0.6733730	0.0961190
13	C	0.6874660	0.6456520	0.0124170
14	C	-1.1403840	-0.6733560	0.0961500
15	C	-0.6874680	0.6456680	0.0124380
16	C	-3.3848450	0.2696020	0.0600180
17	C	-1.4491530	1.8009970	-0.0940010
18	C	-2.5272200	-0.8614380	0.1198000
19	C	-2.8615930	1.6384910	-0.1003310
20	C	-0.7456280	3.0413460	-0.2425900
21	H	-2.9687090	-1.8443910	0.2438210
22	H	-4.6819130	2.7838020	-0.4376580
23	C	-1.5538710	4.1686570	-0.4136620
24	H	-1.1162320	5.1543610	-0.5347900
25	C	-2.9511350	4.0395440	-0.4668430
26	H	-3.5478310	4.9300530	-0.6396530
27	C	-3.6050440	2.8156970	-0.3296890
28	N	-0.0000100	-1.4927550	0.1683860
29	C	0.0000070	-2.9454480	0.2045190
30	H	-0.8838090	-3.2972000	0.7409870
31	H	0.8832040	-3.2971910	0.7420250
32	C	4.8066950	0.0389600	0.1870480
33	C	-4.8067070	0.0390160	0.1871120
34	C	5.7814830	0.8343400	0.8074190
35	H	5.5405070	1.7732820	1.2883090
36	C	7.0536900	0.2736540	0.8303340
37	H	7.9197040	0.7318410	1.2926720
38	C	7.1202860	-0.9937870	0.2130450
39	C	8.2542900	-1.8128350	0.0662580
40	C	-5.7815270	0.8343410	0.8074650
41	H	-5.5406110	1.7732890	1.2883780
42	C	-7.0537270	0.2736270	0.8303400
43	H	-7.9197580	0.7317980	1.2926620
44	C	-7.1202800	-0.9938090	0.2130320
45	C	-8.2542800	-1.8128570	0.0662350
46	S	5.5385810	-1.4569050	-0.3994370
47	S	-5.5385650	-1.4568720	-0.3994540
48	C	9.5160850	-1.3678870	0.5424810

49	C	8.1747670	-3.0884110	-0.5490030
50	C	-8.1747620	-3.0884150	-0.5490650
51	C	-9.5160790	-1.3679270	0.5424660
52	N	10.5395020	-0.9780950	0.9446760
53	N	8.0788530	-4.1341280	-1.0583320
54	N	-8.0788560	-4.1341100	-1.0584410
55	N	-10.5395070	-0.9781390	0.9446350
56	H	3.5478540	4.9300020	-0.6398020
57	H	0.0005930	-3.3782940	-0.8020430

QDTQ in the singlet state (CS; rb3lyp/6-31G(d,p))
Total Energy (Hartree): -3273.3362

Row	Symbol	X	Y	Z
1	H	5.1405620	0.0010660	1.0228380
2	C	4.1760980	-0.0133220	1.5178720
3	C	2.9978040	-0.0283630	0.7214360
4	C	2.9486470	-0.0326360	3.6220680
5	C	1.7455720	-0.0463130	1.3902990
6	C	4.1667330	-0.0197160	2.9036730
7	C	1.7783050	-0.0377740	2.8082720
8	C	0.4522000	-0.0819550	0.7188960
9	H	5.1165070	-0.0112460	3.4287190
10	C	-0.7785990	-0.1209180	1.4771150
11	H	-1.7268640	-0.1519510	0.9571050
12	C	-0.7257830	-0.1179160	2.8569950
13	C	0.5500030	-0.0582500	3.4525750
14	C	-0.9515480	-0.1380520	5.1392870
15	C	0.4180670	-0.0604360	4.8084150
16	C	-0.2260130	-0.0445580	7.4683910
17	C	1.5003800	-0.0480230	5.6756780
18	C	-1.2770270	-0.1351880	6.4818560
19	C	1.2065870	-0.0914370	7.0671900
20	C	2.8101430	-0.0607850	5.0904730
21	H	-2.3064570	-0.1086810	6.8203240
22	H	2.1986660	-0.4235950	8.9687570
23	C	3.8750090	-0.1434550	6.0063920
24	H	4.9038540	-0.1581350	5.6614720
25	C	3.6173970	-0.2588570	7.3722660
26	H	4.4545810	-0.3764630	8.0535230
27	C	2.3191690	-0.2558870	7.9063550
28	N	-1.6541570	-0.1766550	3.9198630
29	C	-0.6000230	0.1250230	8.8225250
30	H	-1.7268640	-0.1519510	-0.9571050

31	C	-0.7785990	-0.1209180	-1.4771150
32	C	0.4522000	-0.0819550	-0.7188960
33	C	0.5500030	-0.0582500	-3.4525750
34	C	1.7455720	-0.0463130	-1.3902990
35	C	-0.7257830	-0.1179160	-2.8569950
36	C	1.7783050	-0.0377740	-2.8082720
37	C	2.9978040	-0.0283630	-0.7214360
38	C	4.1760980	-0.0133220	-1.5178720
39	H	5.1405620	0.0010660	-1.0228380
40	C	4.1667330	-0.0197160	-2.9036730
41	H	5.1165070	-0.0112460	-3.4287190
42	C	2.9486470	-0.0326360	-3.6220680
43	C	-0.9515480	-0.1380520	-5.1392870
44	C	0.4180670	-0.0604360	-4.8084150
45	C	-0.2260130	-0.0445580	-7.4683910
46	C	1.5003800	-0.0480230	-5.6756780
47	C	-1.2770270	-0.1351880	-6.4818560
48	C	1.2065870	-0.0914370	-7.0671900
49	C	2.8101430	-0.0607850	-5.0904730
50	H	-2.3064570	-0.1086810	-6.8203240
51	H	2.1986660	-0.4235950	-8.9687570
52	C	3.8750090	-0.1434550	-6.0063920
53	H	4.9038540	-0.1581350	-5.6614720
54	C	3.6173970	-0.2588570	-7.3722660
55	H	4.4545810	-0.3764630	-8.0535230
56	C	2.3191690	-0.2558870	-7.9063550
57	N	-1.6541570	-0.1766550	-3.9198630
58	C	-0.6000230	0.1250230	-8.8225250
59	C	0.1154750	0.7230150	-9.8908400
60	H	1.1001660	1.1494960	-9.7556610
61	C	-0.5760500	0.8165500	-11.0776990
62	H	-0.1919670	1.2759370	-11.9801990
63	C	-1.8930410	0.2842160	-11.0150030
64	C	-2.8323130	0.2225190	-12.0467270
65	C	0.1154750	0.7230150	9.8908400
66	H	1.1001660	1.1494960	9.7556610
67	C	-0.5760500	0.8165500	11.0776990
68	H	-0.1919670	1.2759370	11.9801990
69	C	-1.8930410	0.2842160	11.0150030
70	C	-2.8323130	0.2225190	12.0467270
71	S	-2.2234400	-0.3233480	-9.3985560
72	S	-2.2234400	-0.3233480	9.3985560
73	C	-2.4910910	0.6920920	-13.3443490
74	C	-4.1348940	-0.2999140	-11.8314650

75	C	-4.1348940	-0.2999140	11.8314650
76	C	-2.4910910	0.6920920	13.3443490
77	N	-5.1972050	-0.7341420	11.6200120
78	N	-2.1835570	1.0871710	14.3980200
79	N	-2.1835570	1.0871710	-14.3980200
80	N	-5.1972050	-0.7341420	-11.6200120
81	C	-3.0980110	-0.2015510	3.7800870
82	H	-3.5218380	0.8071930	3.7118000
83	H	-3.3690220	-0.7619650	2.8819070
84	H	-3.5378900	-0.7113480	4.6399670
85	C	-3.0980110	-0.2015510	-3.7800870
86	H	-3.3690220	-0.7619650	-2.8819070
87	H	-3.5218380	0.8071930	-3.7118000
88	H	-3.5378900	-0.7113480	-4.6399670

QDTQ in the singlet biradical state (SB; BS-ub3lyp/6-31g(d,p))

Total Energy (Hartree): -3273.3408

<S2>: 1.0207

Row	Symbol	X	Y	Z
1	H	4.7003090	0.0428860	1.0222690
2	C	3.7363910	-0.0078010	1.5161690
3	C	2.5666100	-0.0654600	0.7269540
4	C	2.5245750	-0.0780370	3.6286010
5	C	1.3149900	-0.1305730	1.3977810
6	C	3.7302030	-0.0164360	2.9113860
7	C	1.3499860	-0.1268490	2.8146410
8	C	0.0200720	-0.2088200	0.7311470
9	H	4.6821840	0.0263030	3.4313290
10	C	-1.1904170	-0.2868410	1.4772530
11	H	-2.1397850	-0.3456710	0.9604550
12	C	-1.1382710	-0.2860920	2.8743230
13	C	0.1264580	-0.1936220	3.4594310
14	C	-1.3587300	-0.3263100	5.1512540
15	C	-0.0037280	-0.2132000	4.8266990
16	C	-0.6340720	-0.2567730	7.4764960
17	C	1.0784090	-0.1641290	5.6921020
18	C	-1.6778310	-0.3419690	6.5113730
19	C	0.7873360	-0.2158530	7.0837480
20	C	2.3888590	-0.1117830	5.1065730
21	H	-2.7054560	-0.3515710	6.8582160
22	H	1.7978940	-0.4223770	8.9998390
23	C	3.4505060	-0.1286670	6.0190450
24	H	4.4794340	-0.0935780	5.6753090
25	C	3.1999060	-0.2304590	7.3953340

26	H	4.0458970	-0.2843020	8.0739830
27	C	1.9121780	-0.2873720	7.9317530
28	N	-2.0643730	-0.3757930	3.9332330
29	C	-1.0137840	-0.1849940	8.8668520
30	H	-2.1397910	-0.3456630	-0.9604360
31	C	-1.1904250	-0.2868310	-1.4772390
32	C	0.0200690	-0.2088160	-0.7311390
33	C	0.1264400	-0.1936020	-3.4594220
34	C	1.3149830	-0.1305650	-1.3977790
35	C	-1.1382860	-0.2860730	-2.8743090
36	C	1.3499720	-0.1268330	-2.8146380
37	C	2.5666070	-0.0654550	-0.7269570
38	C	3.7363830	-0.0077900	-1.5161780
39	H	4.7003040	0.0428960	-1.0222820
40	C	3.7301880	-0.0164160	-2.9113950
41	H	4.6821670	0.0263290	-3.4313420
42	C	2.5245570	-0.0780140	-3.6286040
43	C	-1.3587560	-0.3262790	-5.1512400
44	C	-0.0037520	-0.2131740	-4.8266900
45	C	-0.6341040	-0.2567560	-7.4764830
46	C	1.0783810	-0.1640990	-5.6920960
47	C	-1.6778630	-0.3419340	-6.5113580
48	C	0.7873000	-0.2158190	-7.0837400
49	C	2.3888330	-0.1117480	-5.1065760
50	H	-2.7054900	-0.3515380	-6.8581970
51	H	1.7978390	-0.4222720	-8.9998470
52	C	3.4504740	-0.1286100	-6.0190570
53	H	4.4794040	-0.0935130	-5.6753280
54	C	3.1998660	-0.2303790	-7.3953470
55	H	4.0458520	-0.2841940	-8.0740030
56	C	1.9121340	-0.2872980	-7.9317580
57	N	-2.0643930	-0.3757650	-3.9332150
58	C	-1.0137950	-0.1850150	-8.8668460
59	C	-0.4007350	0.5023010	-9.9253270
60	H	0.4909450	1.0995250	-9.7867280
61	C	-1.0816420	0.4281880	-11.1353700
62	H	-0.7696280	0.9217690	-12.0478360
63	C	-2.2658280	-0.3363080	-11.0692230
64	C	-3.1695240	-0.6067120	-12.1132130
65	C	-0.4007850	0.5023980	9.9253200
66	H	0.4908610	1.0996690	9.7867180
67	C	-1.0817060	0.4282850	11.1353550
68	H	-0.7697310	0.9219090	12.0478120
69	C	-2.2658520	-0.3362720	11.0692140

70	C	-3.1695450	-0.6066990	12.1132000
71	S	-2.4951870	-0.9607130	-9.4418330
72	S	-2.4951800	-0.9606960	9.4418270
73	C	-2.9106860	-0.1134070	-13.4191990
74	C	-4.3484080	-1.3645440	-11.8966080
75	C	-4.3483950	-1.3645830	11.8965960
76	C	-2.9107380	-0.1133640	13.4191810
77	N	-5.3116630	-1.9901010	11.6877640
78	N	-2.6737670	0.3063680	14.4818880
79	N	-2.6736880	0.3062990	-14.4819110
80	N	-5.3117030	-1.9900190	-11.6877750
81	C	-3.5075430	-0.4354760	3.7947570
82	H	-3.9561160	0.5630550	3.7346390
83	H	-3.7662040	-0.9949360	2.8924740
84	H	-3.9342880	-0.9624500	4.6508990
85	C	-3.5075630	-0.4354440	-3.7947320
86	H	-3.7662220	-0.9949080	-2.8924510
87	H	-3.9561330	0.5630880	-3.7346070
88	H	-3.9343140	-0.9624130	-4.6508740

QDTQ in the triplet state (TB; ub3lyp/6-31g(d,p))

Total Energy (Hartree): - 3273.3386

<S2>: 2.0466

Row	Symbol	X	Y	Z
1	H	5.0874840	-0.2584580	1.0220240
2	C	4.1239120	-0.1976070	1.5155360
3	C	2.9577420	-0.1234320	0.7291090
4	C	2.9175000	-0.1231380	3.6310630
5	C	1.7066510	-0.0439190	1.4006770
6	C	4.1181570	-0.2010180	2.9143020
7	C	1.7428260	-0.0418850	2.8171710
8	C	0.4102840	0.0299870	0.7358150
9	H	5.0701110	-0.2647590	3.4323170
10	C	-0.7942940	0.0977210	1.4774270
11	H	-1.7446820	0.1525180	0.9616390
12	C	-0.7424890	0.0971970	2.8807040
13	C	0.5210760	0.0379770	3.4621760
14	C	-0.9643340	0.1023700	5.1564170
15	C	0.3903360	0.0446010	4.8334840
16	C	-0.2345220	0.0986940	7.4791210
17	C	1.4718780	-0.0260960	5.6978630
18	C	-1.2802990	0.1370650	6.5222860
19	C	1.1784080	-0.0259800	7.0897590
20	C	2.7800730	-0.1293800	5.1126890

21	H	-2.3007780	0.2516230	6.8721680
22	H	2.1623000	-0.2961280	9.0135750
23	C	3.8315020	-0.2539550	6.0249040
24	H	4.8577830	-0.3404000	5.6821160
25	C	3.5729450	-0.3024750	7.4054460
26	H	4.4098720	-0.4375870	8.0841280
27	C	2.2907290	-0.2030650	7.9423890
28	N	-1.6723600	0.1291440	3.9384330
29	C	-0.6019460	0.2175220	8.8789240
30	H	-1.7446820	0.1525180	-0.9616390
31	C	-0.7942940	0.0977210	-1.4774270
32	C	0.4102840	0.0299870	-0.7358150
33	C	0.5210760	0.0379770	-3.4621760
34	C	1.7066510	-0.0439190	-1.4006770
35	C	-0.7424890	0.0971970	-2.8807040
36	C	1.7428260	-0.0418850	-2.8171710
37	C	2.9577420	-0.1234320	-0.7291090
38	C	4.1239120	-0.1976070	-1.5155360
39	H	5.0874840	-0.2584580	-1.0220240
40	C	4.1181570	-0.2010180	-2.9143020
41	H	5.0701110	-0.2647590	-3.4323170
42	C	2.9175000	-0.1231380	-3.6310630
43	C	-0.9643340	0.1023700	-5.1564170
44	C	0.3903360	0.0446010	-4.8334840
45	C	-0.2345220	0.0986940	-7.4791210
46	C	1.4718780	-0.0260960	-5.6978630
47	C	-1.2802990	0.1370650	-6.5222860
48	C	1.1784080	-0.0259800	-7.0897590
49	C	2.7800730	-0.1293800	-5.1126890
50	H	-2.3007780	0.2516230	-6.8721680
51	H	2.1623000	-0.2961280	-9.0135750
52	C	3.8315020	-0.2539550	-6.0249040
53	H	4.8577830	-0.3404000	-5.6821160
54	C	3.5729450	-0.3024750	-7.4054460
55	H	4.4098720	-0.4375870	-8.0841280
56	C	2.2907290	-0.2030650	-7.9423890
57	N	-1.6723600	0.1291440	-3.9384330
58	C	-0.6019460	0.2175220	-8.8789240
59	C	0.0612010	0.8801460	-9.9171900
60	H	0.9901620	1.4135510	-9.7624060
61	C	-0.6156050	0.8647640	-11.1362070
62	H	-0.2657430	1.3496640	-12.0396740
63	C	-1.8422900	0.1751700	-11.0874510
64	C	-2.7586230	-0.0210720	-12.1411620

65	C	0.0612010	0.8801460	9.9171900
66	H	0.9901620	1.4135510	9.7624060
67	C	-0.6156050	0.8647640	11.1362070
68	H	-0.2657430	1.3496640	12.0396740
69	C	-1.8422900	0.1751700	11.0874510
70	C	-2.7586230	-0.0210720	12.1411620
71	S	-2.1180220	-0.4617760	-9.4717660
72	S	-2.1180220	-0.4617760	9.4717660
73	C	-2.4667840	0.4816320	-13.4360250
74	C	-3.9814710	-0.7103760	-11.9437150
75	C	-3.9814710	-0.7103760	11.9437150
76	C	-2.4667840	0.4816320	13.4360250
77	N	-4.9822860	-1.2801940	11.7521090
78	N	-2.2020810	0.9072830	14.4898980
79	N	-2.2020810	0.9072830	-14.4898980
80	N	-4.9822860	-1.2801940	-11.7521090
81	C	-3.1111360	0.2552370	3.7993440
82	H	-3.4268890	1.3030590	3.7328570
83	H	-3.4401750	-0.2712990	2.9002210
84	H	-3.6025810	-0.2070900	4.6581280
85	C	-3.1111360	0.2552370	-3.7993440
86	H	-3.4401750	-0.2712990	-2.9002210
87	H	-3.4268890	1.3030590	-3.7328570
88	H	-3.6025810	-0.2070900	-4.6581280