

Electronic Supplementary Information

Improving photovoltaic performance of perovskite solar cells through the molecular design of donor-acceptor polymeric hole-transport materials

D. S. Zamoretskov, A. N. Zhivchikova, I. E. Kuznetsov, M. M. Tepliakova, N.G. Nikitenko, I. A. Konushkin, M. V. Gapanovich, D. A. Chernyayev, E.O. Perepelitsina, D. K. Sagdullina, A.V. Akkuratov

Materials and Instruments

All solvents were purchased from Merck or Acros Organics and used as received. Monomer BDT was synthesized as reported previously ¹.

The thermal properties of the polymers were investigated by thermal gravimetry analysis and differential scanning calorimetry using NETZSCH STA 449 F3 Jupiter instrument in inert atmosphere (helium) with a heating rate of 15°C.

Absorption and photoluminescence spectra for solutions and thin films deposited by spin-coating from 1×10^{-2} M solutions on quartz substrates were measured in UV-visible region (250-800 nm) on fiber optical spectrometer OPTOSKY ATP 2400.

Electrochemical measurements were carried out according to the previously reported method ² using an ELINS P-20-X instrument (Electrochemical Instruments, Russia), except of using chlorobenzene for deposition of all films.

AFM measurements were performed using an NTEGRA PRIMA instrument (NT-MDT, Russia).

DFT calculations

The geometry of molecules was optimized using the PBE density functional method ³ with an extended basis set for valence electrons and the SBK ^{4,5} using the «Priroda» soft ^{6,7}. Calculation of the energy levels of the frontier molecular orbitals of molecules carried out using the Gaussian-03 program package ⁸ in 6-31+G(d) basis set with the hybrid functional B3LYP ^{9,10}. All calculations were carried out for isolated molecules in the gas phase.

Fabrication of hole-only devices

SCLC devices were fabricated on glass substrates with photo-lithographically defined bottom ITO electrode. PEDOT:PSS (PH 1000, Heraeus Clevis) was deposited by spin-coating. The substrates were subsequently dried at 160°C for 10 min. Thin films of all compounds were deposited by spin coating from chlorobenzene solutions giving film thicknesses in the range of 150-230 nm. After that, MoO₃ and Ag were successively deposited by thermal evaporation in a vacuum chamber (6×10^{-6} mbar) to form the top electrode. The same procedure was performed for devices, where the films were additionally annealed at 150 °C. The film thickness was recorded by making a thin

scratch on the top of films. Subsequently, the AFM was scanned across the cut and the film thickness could thus be extracted from the resulting image.

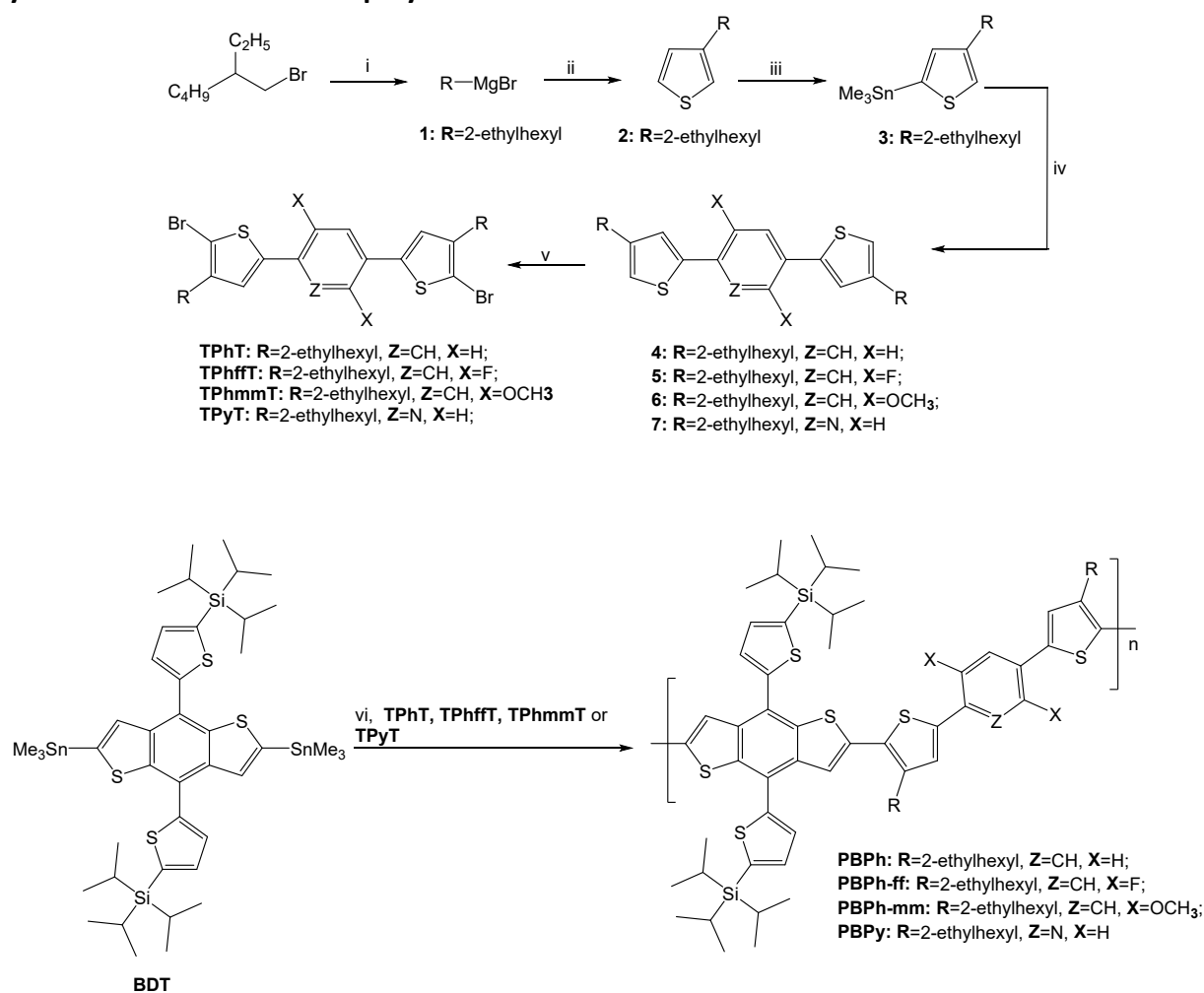
Fabrication of perovskite solar cells

Glass/ITO substrates (Kintec, 15 Ω /sq.) were cleaned with ultrasonication in acetone, water, and isopropanol for 15 minutes. Before deposition of ETL substrates were exposed to air plasma at 50% power for 5 minutes. The SnO₂ (15% nanoparticles in H₂O, Alfa Aesar) was spin-coated at 4000 rpm under ambient conditions. Further films were annealed at 175°C for 30 min, introduced into glovebox and additionally annealed at 100°C for 5 min. The passivating layer [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (0.2 mg/mL in chlorobenzene) was spin-coated at 3000 rpm and annealed at 100°C for 10 min. The compounds CH₃NH₃I and PbI₂ were dissolved in the mixture of DMF and NMP (4:1) to give the 1.4 M solution of the CH₃NH₃PbI₃ ink. The perovskite ink was spin-coated at 4000 rpm, quenched with antisolvent at 20 sec, and left to dry at 4000 rpm for 40 sec, and afterwards without rotation at room temperature for 20 min. Next, the devices were slowly heated to 80°C and annealed at this temperature for 5 minutes. A solution of polymers in chlorobenzene was applied over the perovskite film by spin-coating at 2000 rpm. The optimal deposition conditions (concentration, spin-coating rate, solvent) for each hole-transport material were found from preliminary experiments. The thickness of films were 140 nm, 155 nm, 180 nm, 160 nm for **PBPh**, **PBPh-ff**, **PBPh-mm**, **PBPy**, respectively. The top electrode containing MoO_x (10 nm) and Ag (100 nm) was deposited through a shadow mask using thermal evaporation under reduced pressure (10⁻⁵ mbar), whereby the active area of the photovoltaic cells was 0.1 cm².

Fabrication of solar cells for the stability evaluation

The ITO substrates were ultrasonicated with isopropanol, DI water, acetone, and exposed to plasma cleaning (50 W) for 10 minutes. Suspension of SnO₂ (10% in DI water) was filtered through 0.45 μ m PES, spin-coated at 4000 rpm for 40 sec, and annealed at 175°C for 20 min in the air. After this step, the samples were transferred into the glovebox. The [6,6]-phenyl-C₆₁-butyric acid (PCBA) was spin-coated statically at 3000 rpm and annealed at 100°C for 10 minutes. The solution of 1.2 M perovskite ink was prepared by mixing the following powder ratios: 442.6 mg of PbI₂, 528.6 mg of PbBr₂, 106.2 mg of CsI, 342.6 mg of FAI, in 2 mL of DMF solvent followed by filtration through 0.45 μ m PTFE. The filtered perovskite ink (50 μ L) was deposited at 3000 rpm, quenched with 75 μ L ethylacetate antisolvent at 10 s, and annealed at 100°C for 10 min. The 45 μ L of **PBPh**, **PBPh-ff**, **PBPh-mm**, **PBPy** (all 5 mg mL⁻¹ in chlorobenzene) were warmed up to 100°C and spin-coated on the top of the perovskite layer at 4000 rpm with rotation for 30 s. 30 nm of vanadium (V) oxide was thermally evaporated under reduced pressure of 10⁻⁵ mbar. The part of the upper sputtered layer was removed to ensure contact with the cathode. Finally, 120 nm of top metal Au electrode was thermally evaporated through the shadow mask finalizing the area of devices 0.16 cm². Encapsulation of devices was performed with kapton-tape and UV-cured epoxy resin. The stability of solar cells was studied under ambient conditions (30°C, 60% humidity).

Synthesis of monomers and polymers



Scheme 1S. Synthesis of **TPhT**, **TPhffT**, **TPhmmT**, and **TPyT** monomers and polymers **PBPh**, **PBPh-ff**, **PBPh-mm**, and **PBPy**.

(2-ethylhexyl)magnesium bromide (1). In a 1000 mL three-necked flask equipped with a condenser and dropping funnel in an inert atmosphere, magnesium (12.4 g; 517 mmol) with two small crystals of iodine was stirred for 20 minutes upon heating until iodine vapors appeared. Thereafter, 100 mL of dry tetrahydrofuran (THF) was added to the flask. Then a solution of 2-ethylhexyl bromide (25.0 g; 129 mmol) in 200 mL THF was added dropwise. The reaction mixture was refluxed for 3-4 hours. The yield of the compound **1** found from titration with H₂SO₄ (0.1N) was 86% (24.3 g).

3-(2-ethylhexyl)thiophene (2). A solution of 3-bromothiophene (24.3 g; 112 mmol) in 100 mL of THF and dichloro[1,3-bis (diphenylphosphino)propane] nickel as a catalyst (0.635 g, 1.12 mmol) were placed into 1000 mL three-necked round-bottom flask equipped with dropping funnel in an inert atmosphere. Then, compound **1** (24.3 g; 112 mmol) was added dropwise within 1.5 h at 0°C (ice bath). The resulting reaction mixture was stirred for 2-3 hours at room temperature. After cooling the mixture to 5°C, 200 mL of a 2M hydrochloric acid solution was added. The mixture was transferred to the separating funnel and the product was extracted three times with

chloroform (3×100 mL). The organic phase was washed with 300 mL of saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was evaporated on a rotary evaporator. The desired product was obtained by distillation in a vacuum (108-110°C, P ≈ 3.4 mmHg). Compound **2** was obtained as colorless oil with the yield of 60.0 % (13.27 g). ¹H NMR (CDCl₃, 500 MHz, δ): 7.25 (m, 1H); 6.93 (m, 2H); 2.58 (d, 2H; J= 6.88 Hz); 1.57 (m, 1H); 1.34-1.21 (m, 8H); 0.94-85 (m, 6H) ppm.

(4-(2-ethylhexyl)thiophen-2-yl)trimethylstannane (3). Compound **2** (10 g; 51 mmol) in dry THF (125 mL) was placed into a 250 mL three-neck round-bottom flask, which was previously evacuated/backfilled with argon three times. The flask was cooled to -78 °C in an acetone bath, and the *n*-butyllithium solution (14.1 g; 51 mmol; 2.5 M in *n*-hexane) was added dropwise. The mixture was stirred at -50 °C for 4 h. Then, the solution of a trimethylchlorostannane (10.6 g; 51 mmol) in 10 mL of THF was added at -78°C. The mixture was stirred for 2 h followed by warming to room temperature. THF was removed on a rotary evaporator to give compound **3** as a light-yellow oil – 16.85 g (yield 92.0%). Compound **3** was used without further purification. ¹H NMR (CDCl₃, 500 MHz, δ): 7.19 (s, 1H); 6.99 (s, 1H); 2.60 (d, 2H; J= 6.84 Hz); 1.57 (m, 1H); 1.34-1.21 (m, 8H); 0.92-0.84 (m, 6H); 0.37 (s, 9H) ppm.

2,5-bis(4-(2-ethylhexyl)thiophen-2-yl)benzene (4). Compound **3** (4.6 g; 13 mmol), 2,5-dibromobenzene (1 g; 4 mmol), palladium acetate (0.006 g; 3 mmol), and triphenylphosphine (0.006 g; 2 mmol) were dissolved in toluene (15 mL) in a 50 mL three-necked round-bottom flask equipped with a condenser. The solution was deaerated and then stirred at reflux (110°C) for 24 h. The reaction mixture was cooled to room temperature and the solvent was removed on a rotary evaporator. The target compound was purified by column chromatography using hexane as eluent giving 0.9 g of compound **4** (yield 45%). ¹H NMR (CDCl₃, 500 MHz, δ): 7.60 (s, 4H); 7.16 (s, 2H); 6.87 (s, 2H); 2.57 (d, 4H; J= 6.94 Hz); 1.62 (m, 2H); 1.39-1.32 (m, 16H); 0.94-0.86 (m, 12H) ppm.

5,5'-(2,5-difluoro-1,4-phenylene)bis(3-(2-ethylhexyl)thiophene) (5). Compound **5** was prepared according to the procedure described for compound **4** using compound **3** (2 g; 5.5 mmol), 1,4-dibromo-2,5-difluorobenzene (0.5 g; 1.8 mmol), palladium acetate catalyst (0.003 g; 1.5 mmol), triphenylphosphine (0.006 g; 1 mmol) and toluene 15 mL. The target compound was purified by column chromatography using hexane as eluent that gave of compound **5** 0.4 g (yield 43%). ¹H NMR (CDCl₃, 500 MHz, δ): 7.35-7.33 (t, 2H; J₁= 9.34 Hz, J₂= 8.93 Hz); 7.29 (s, 2H); 6.94 (s, 2H); 2.55 (d, 4H; J= 6.93 Hz); 1.57 (m, 2H); 1.32-1.24 (m, 16H); 0.89-0.85 (m, 12H) ppm.

5,5'-(2,5-dimethoxy-1,4-phenylene)bis(3-(2-ethylhexyl)thiophene) (6). Compound **6** was prepared according to the procedure described for compound **4** using compound **3** (3.6 g; 10 mmol), 1,4-dibromo-2,5-dimethoxybenzene (1 g; 3.4 mmol), palladium acetate catalyst (0.006 g; 3 mmol), triphenylphosphine (0.006 g; 2 mmol) and toluene 15 mL. The target compound was purified by column chromatography using hexane as eluent giving 0.9 g of compound **6** (yield 50%). ¹H NMR

(CDCl₃, 500 MHz, δ): 7.35 (s, 2H); 7.24 (s, 2H); 6.93 (s, 2H); 3.96 (s, 6H); 2.61 (d, 4H; J = 6.84 Hz); 1.65 (m, 2H); 1.38-1.28 (m, 16H); 0.94-0.91 (t, 12H; J = 7.43 Hz) ppm.

2,5-bis(4-(2-ethylhexyl)thiophen-2-yl)pyridine (7). Compound **7** was prepared according to the procedure described for compound **4** using compound **3** (3 g; 8 mmol), 2,5-dibromopyridine (1 g; 4 mmol), palladium acetate (0.006 g; 3 mmol), triphenylphosphine (0.006 g; 2 mmol), and toluene (15 mL). The target compound was purified by column chromatography using hexane as eluent giving 1.3 g of compound **7** (yield 67%). ¹H NMR (CDCl₃, 500 MHz, δ): 8.83 (s, 1H); 7.85-7.83 (dd, 1H; J_1 = 2.38 Hz, J_2 = 5.94 Hz); 7.64-7.62 (d, 1H; J = 7.73 Hz); 7.44 (s, 1H); 7.19 (s, 1H); 7.00 (s, 1H); 6.94 (s, 1H); 2.60 (d, 4H; J = 6.84 Hz); 1.61 (m, 2H); 1.39-1.32 (m, 16H); 0.94-0.91 (m, 12H) ppm.

2,5-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzene (TPhT). In a round-bottom flask for 100 mL, the solution of compound **4** (0.9 g; 1.93 mmol) in chloroform 25 mL was placed. *N*-bromosuccinimide (0.69 g; 3.9 mmol) was added portionwise. The reaction mixture was stirred for 4 hours at room temperature. The solvent was then removed on a rotary evaporator and 30 mL of ethanol was added to the residue. The precipitate was filtered, washed with ethanol (50 mL) and dried. The yield of the white crystalline powder of **TPhT** was 95% (1.1 g). According to HPLC analysis, the purity of the compound was more than 99%. ¹H NMR (CDCl₃, 500 MHz, δ): 7.52 (s, 4H); 7.01 (s, 2H); 2.54 (d, 4H; J = 7.23 Hz); 1.67 (m, 2H); 1.38-1.30 (m, 16H); 0.95-0.91 (m, 12H) ppm. NMR ¹³C (CDCl₃, 126 MHz, δ): 142.73; 142.49; 133.12; 125.81; 124.55; 109.14; 40.00; 33.94; 32.50; 28.81; 25.69; 23.06; 14.14; 10.85 ppm.

5,5'-(2,5-difluoro-1,4-phenylene)bis(2-bromo-3-(2-ethylhexyl)thiophene) (TPh-fft). **TPh-fft** monomer was prepared according to the method described for **TPhT** using compound **6** (0.4 g; 0.8 mmol) in 10 mL of chloroform and *N*-bromosuccinimide (0.3 g; 1.6 mmol). The **TPh-fft** monomer was obtained as a yellow crystalline substance – 0.6 g (94 % yield). According to HPLC analysis, the purity of the compound was more than 98.5 %. ¹H NMR (CDCl₃, 500 MHz, δ): 7.33-7.29 (t, 2H; J_1 = 9.21 Hz, J_2 = 8.82 Hz); 7.17 (s, 2H); 2.55 (d, 4H; J = 7.23 Hz); 1.67 (m, 2H); 1.38-1.29 (m, 16H); 0.95-0.90 (m, 12H) ppm. ¹³C (CDCl₃, 126 MHz, δ): 155.80; 153.83; 142.21; 134.78; 128.12; 121.55-121.35; 114.79-114.55; 111.53; 39.99; 33.84; 32.48; 28.78; 25.69; 23.05; 14.12; 10.83 ppm. ¹⁹F (CDCl₃, 470 MHz, δ): -118.90 (t, 2F) ppm.

5,5'-(2,5-dimethoxy-1,4-phenylene)bis(2-bromo-3-(2-ethylhexyl)thiophene) (TPh-mmT). **TPh-mmT** monomer was prepared according to the method described for **TPhT** using compound **7** (0.9 g; 1.7 mmol) in 25 mL of chloroform and *N*-bromosuccinimide (0.61 g; 3.4 mmol). The **TPh-mmT** monomer was obtained as a yellow crystalline substance – 0.55 g (48 % yield). According to HPLC analysis, the purity of the compound was more than 98.5 %. ¹H NMR (CDCl₃, 500 MHz, δ): 7.17 (s, 4H); 3.97 (s, 6H); 2.56 (d, 4H; J = 7.15 Hz); 1.69 (m, 2H); 1.39-1.32 (m, 16H); 0.95-0.91 (m, 12H) ppm. ¹³C (CDCl₃, 126 MHz, δ): 149.91; 140.78; 137.80; 126.14; 122.61; 110.96; 56.49; 40.01; 33.83; 32.47; 28.78; 25.71; 23.10; 14.16; 10.88 ppm.

2,5-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)pyridine (TPyT). **TPyT** monomer was prepared according to the method described for **TPhT** using compound **7** (1.3 g; 2.85 mmol) in 40 mL of chloroform and *N*-bromosuccinimide (0.97 g; 5.7 mmol). The **TPyT** monomer was obtained as a yellow crystalline substance – 1.2 g (66 % yield). According to HPLC analysis, the purity of the compound was more than 98%. ¹H NMR (CDCl₃, 500 MHz, δ): 8.70 (m, 1H); 7.75-7.72 (dd, 1H; $J_1=2.28$ Hz, $J_2=6.04$ Hz); 7.54 (d, 1H; $J=7.53$ Hz); 7.25 (s, 1H); 7.02 (s, 1H); 2.54 (d, 4H; $J=7.13$ Hz); 1.68 (m, 2H); 1.38-1.31 (m, 16H); 0.95-0.91 (m, 12H) ppm. ¹³C NMR (CDCl₃, 126 MHz, δ): 150.75; 146.07; 143.36; 142.76; 142.59; 139.41; 132.95; 128.12; 125.78; 125.29; 118.01; 112.93; 110.12; 40.01, 39.99; 34.02; 33.88; 32.49; 28.82, 28.89; 25.70; 23.08; 14.16; 10.87 ppm.

Polymer PBPh. The monomers **TPhT** (0.15 g, 0.24 mmol) and **BDT** (0.239 g, 0.24 mmol) were introduced into a 50 mL round-bottom two-necked flask equipped with a reversed condenser and thermometer. Anhydrous toluene (15 mL), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.012 mmol) and tris(*o*-tolyl)phosphine (10 mg, 0.033 mmol) were added. The reaction mixture was deaerated, immersed in an oil bath and heated at reflux for 10–12 hours. Then the reaction mixture was cooled down to room temperature, and the polymer was precipitated by the addition of 30 mL of methanol. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, acetone, chloroform, and chlorobenzene. The chlorobenzene fraction was concentrated to ~20 mL and the final polymer was obtained by precipitating into methanol followed by drying in a vacuum. The total yield of the purified polymer **PBPh** was 39%. $M_w = 22.7$ kDa, $M_w/M_n = 2.0$.

Polymer PBPh-ff. The polymer **PBPh-ff** was synthesized according to the procedure described for **PBPh** using monomers **TPh-ffT** (0.15 g, 0.23 mmol), **BDT** (0.226 g, 0.23 mmol), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.012 mmol), and tris(*o*-tolyl)phosphine (10 mg, 0.033 mmol). Polymer **PBPh-ff** was purified and isolated in the same way as **PBPh**. The total yield of **PBPh-ff** was 39%. $M_w = 44.9$ kDa, $M_w/M_n = 2.5$

Polymer PBPh-mm. The polymer **PBPh-mm** was synthesized according to the procedure described for **PBPh** using monomers **TPh-mmT** (0.177 g, 0.26 mmol), **BDT** (0.257 g, 0.26 mmol), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.012 mmol), and tris(*o*-tolyl)phosphine (10 mg, 0.033 mmol). Polymer **PBPh-mm** was purified and isolated in the same way as **PBPh**. The total yield of **PBPh-mm** was 49%. $M_w = 61$ kDa, $M_w/M_n = 1.8$

Polymer PBPy. The polymer **PBPy** was synthesized according to the procedure described for **PBPh** using monomers **TPyT** (0.15 g, 0.24 mmol), **BDT** (0.239 g, 0.24 mmol), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.012 mmol), and tris(*o*-tolyl)phosphine (10 mg, 0.033 mmol) in this case. Polymer **PBPy** was purified and isolated in the same way as **PBPh**. The total yield of **PBPy** was 90%. $M_w = 71$ kDa, $M_w/M_n = 2.7$

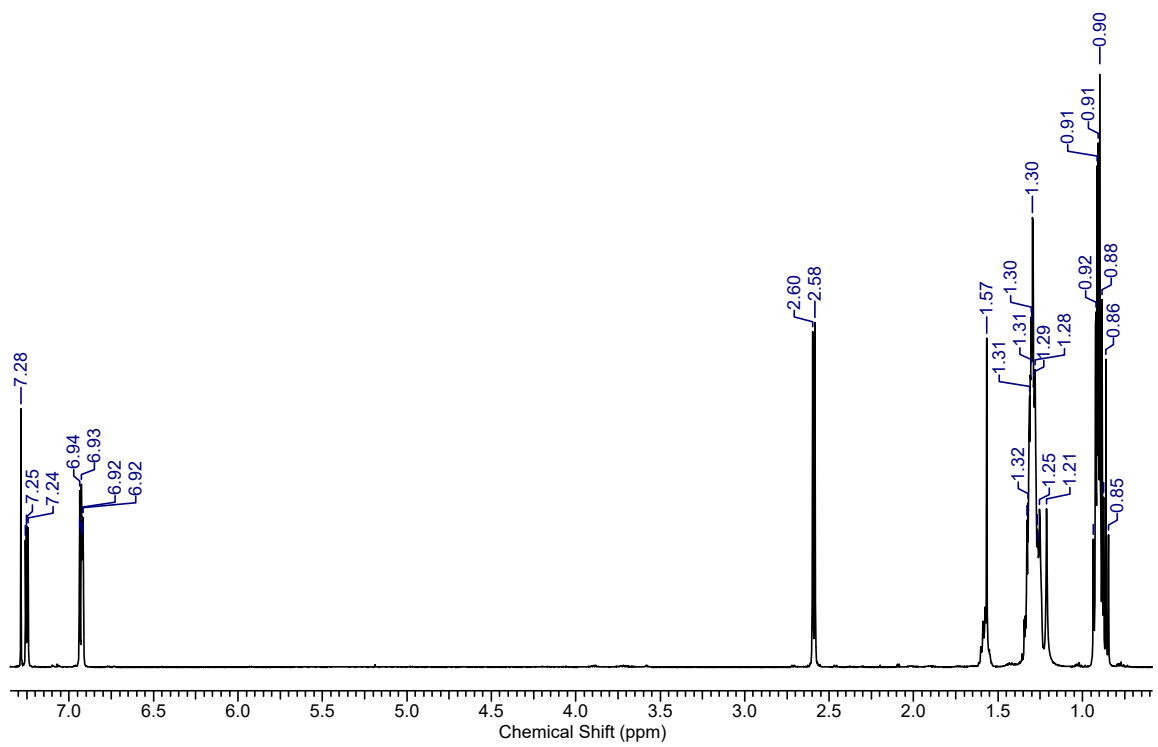


Figure S1. ^1H NMR spectrum of compound **2**.

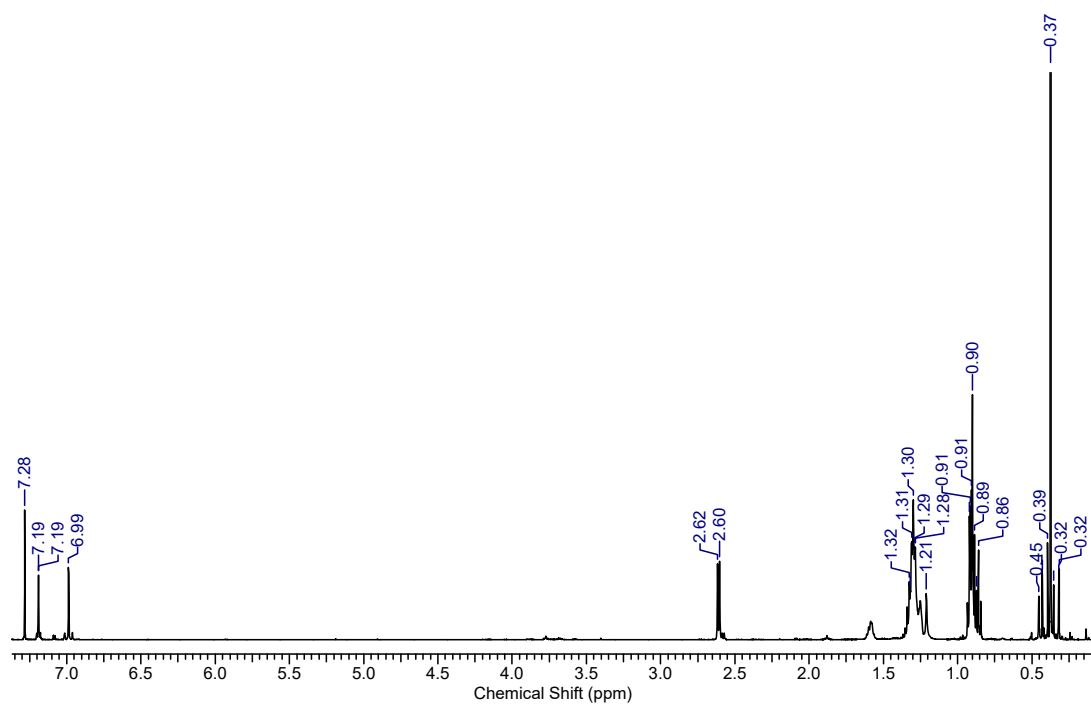


Figure S2. ^1H NMR spectrum of compound **3**.

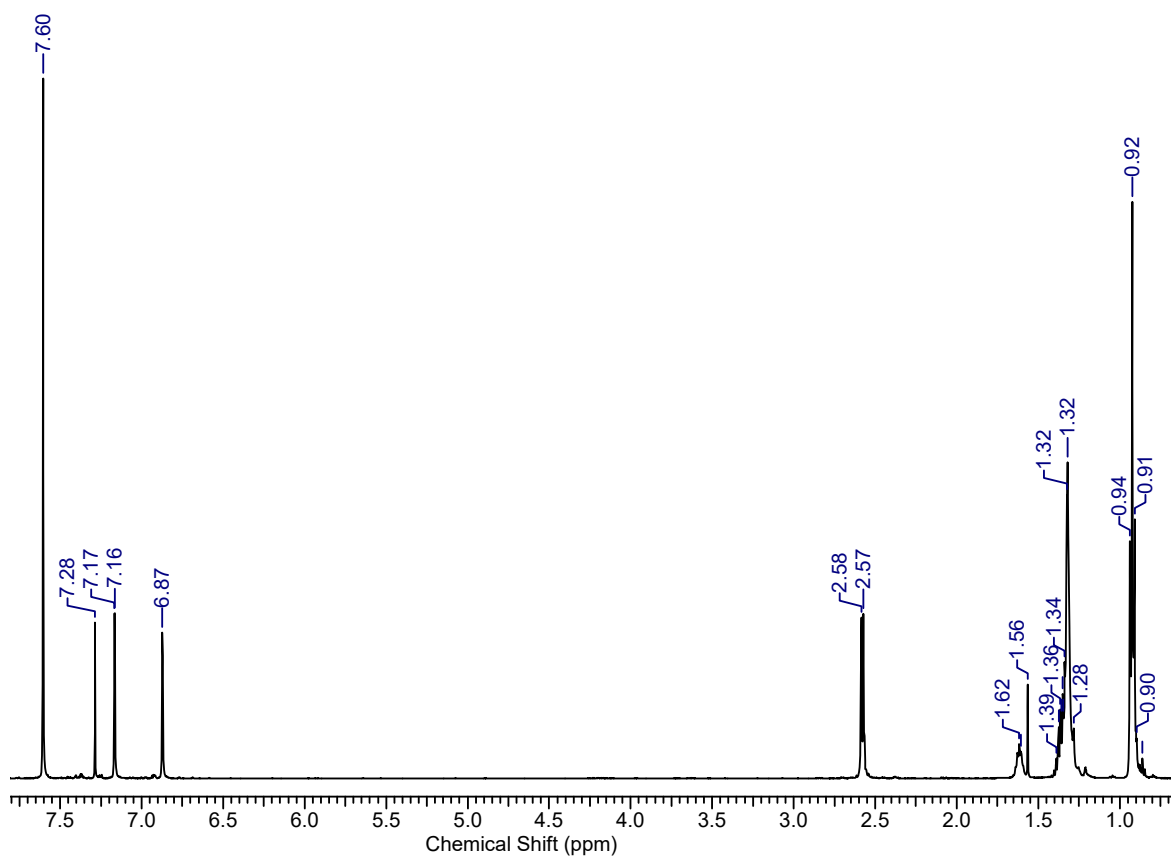


Figure S3. ^1H NMR spectrum of compound **4**.

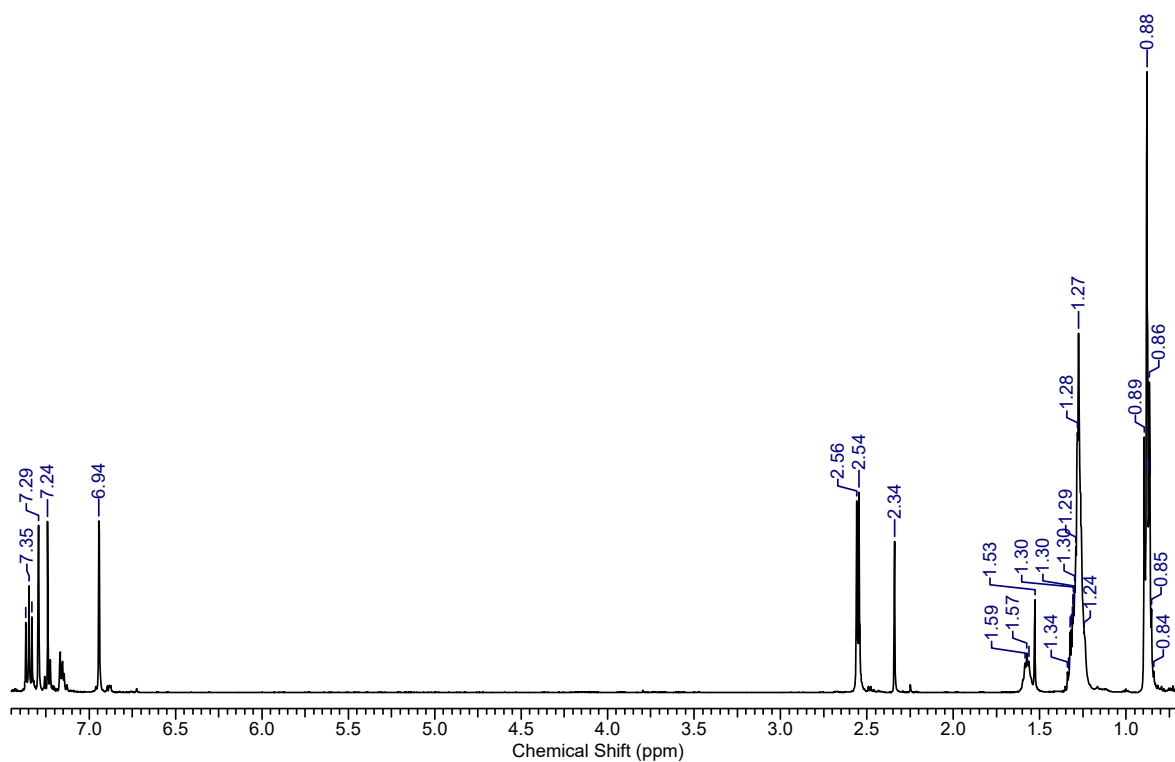


Figure S4. ^1H NMR spectrum of compound **5**.

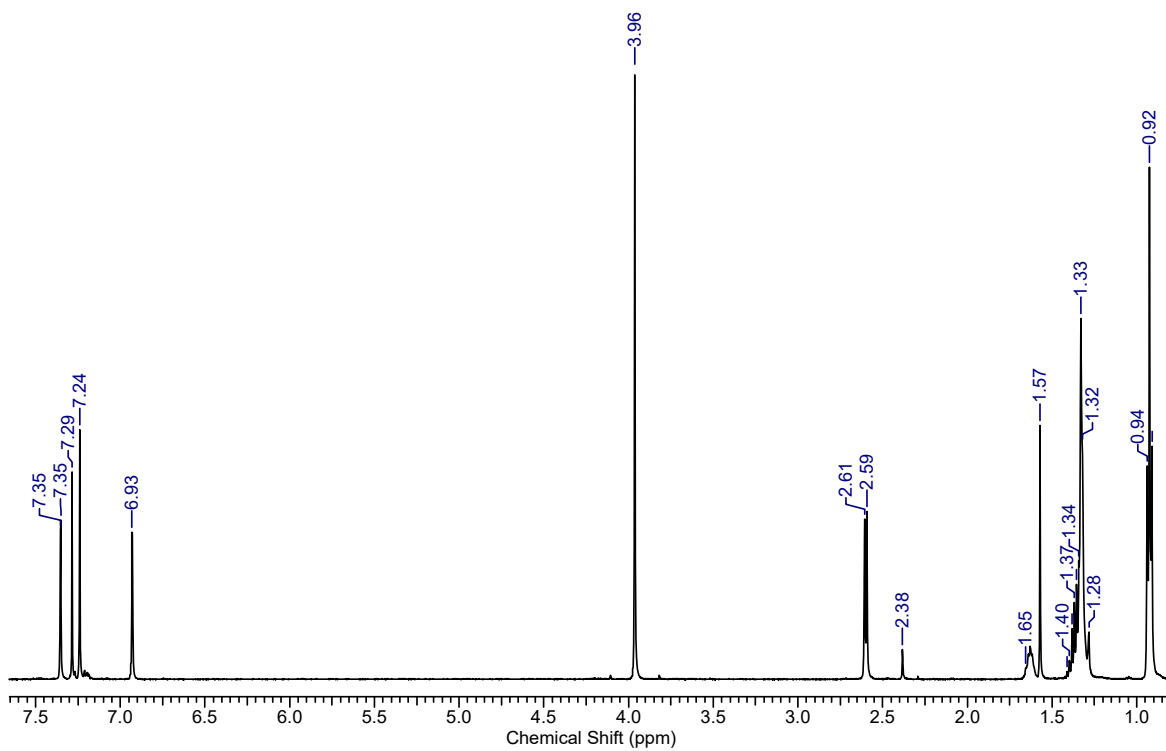


Figure S5. ^1H NMR spectrum of compound **6**.

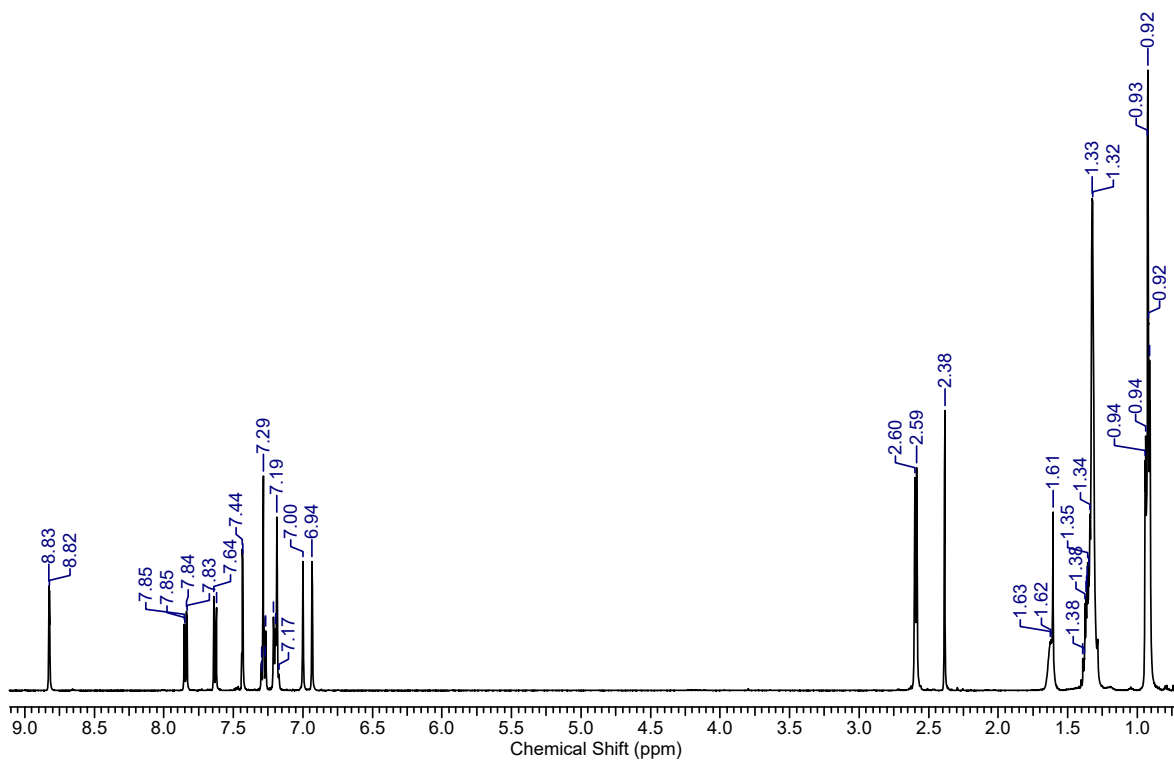


Figure S6. ^1H NMR spectrum of compound **7**.

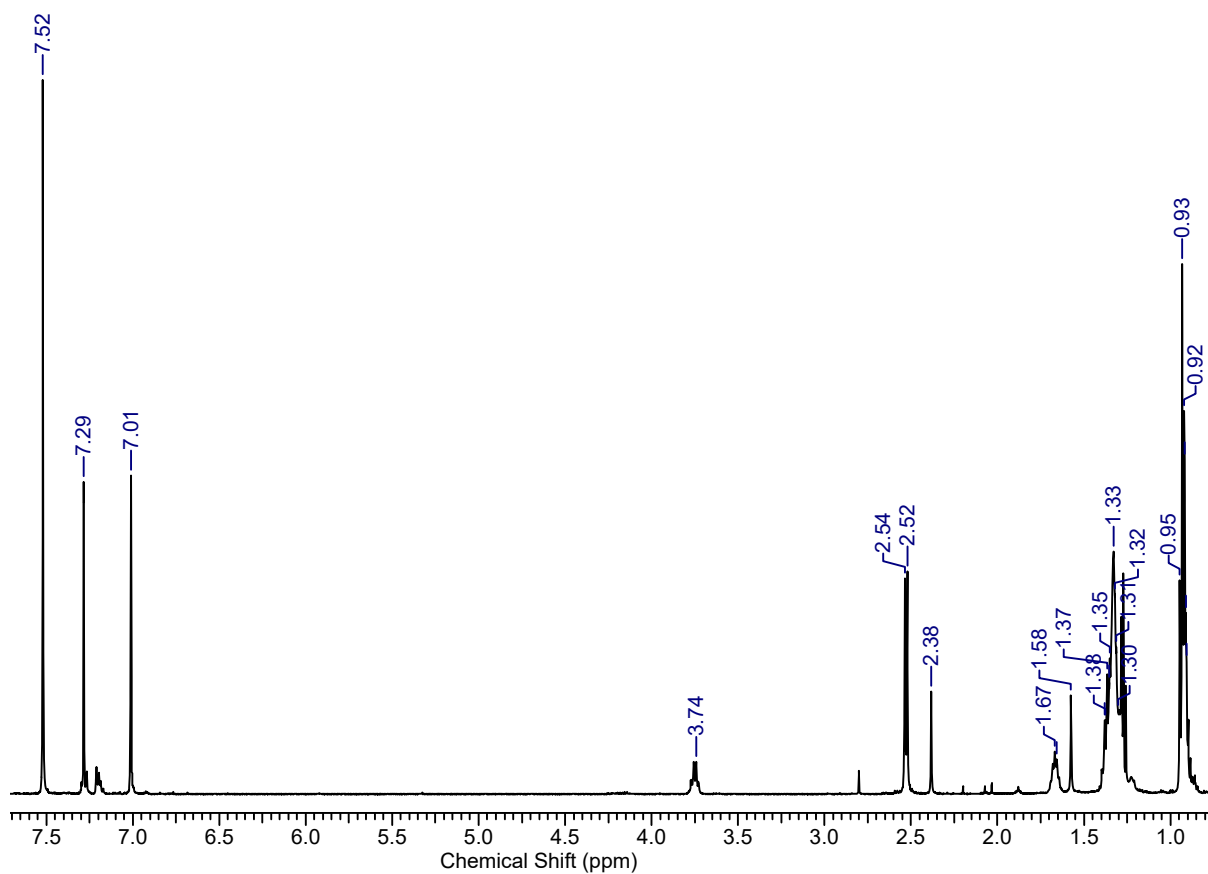


Figure S7. ^1H NMR spectrum of compound TPhT.

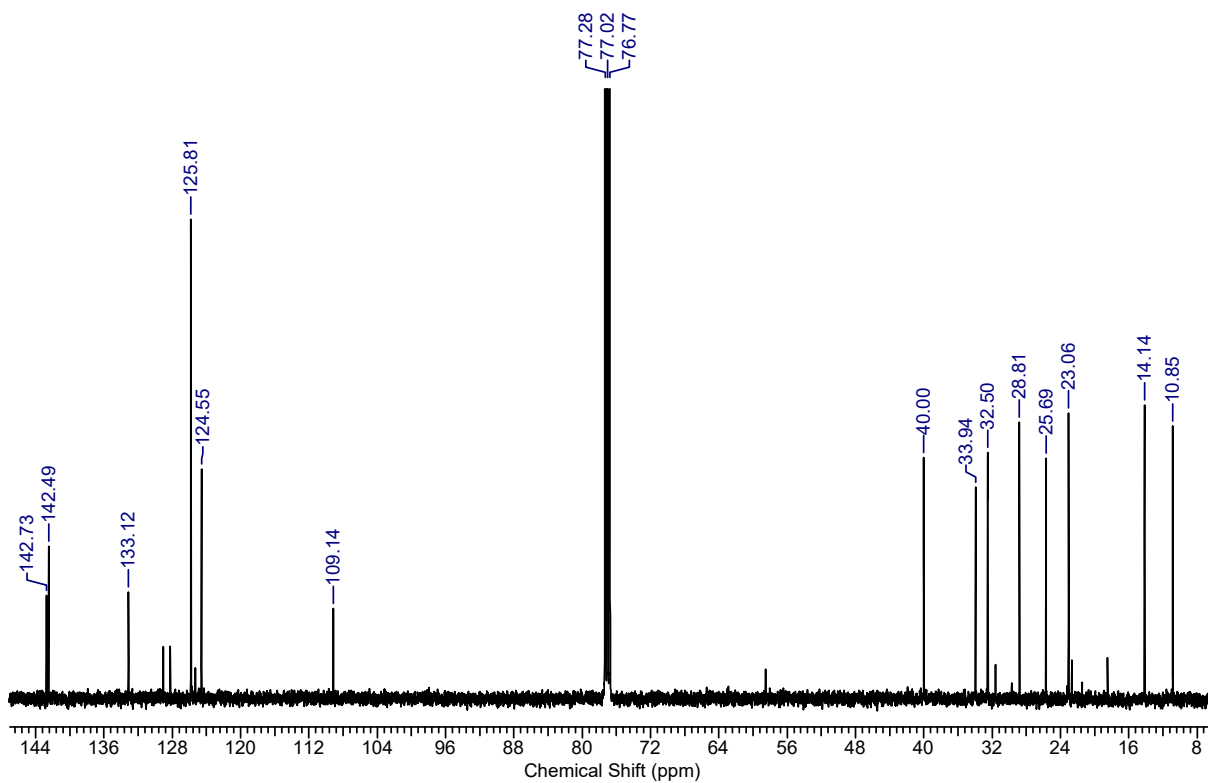


Figure S8. ^{13}C NMR spectrum of compound TPhT.

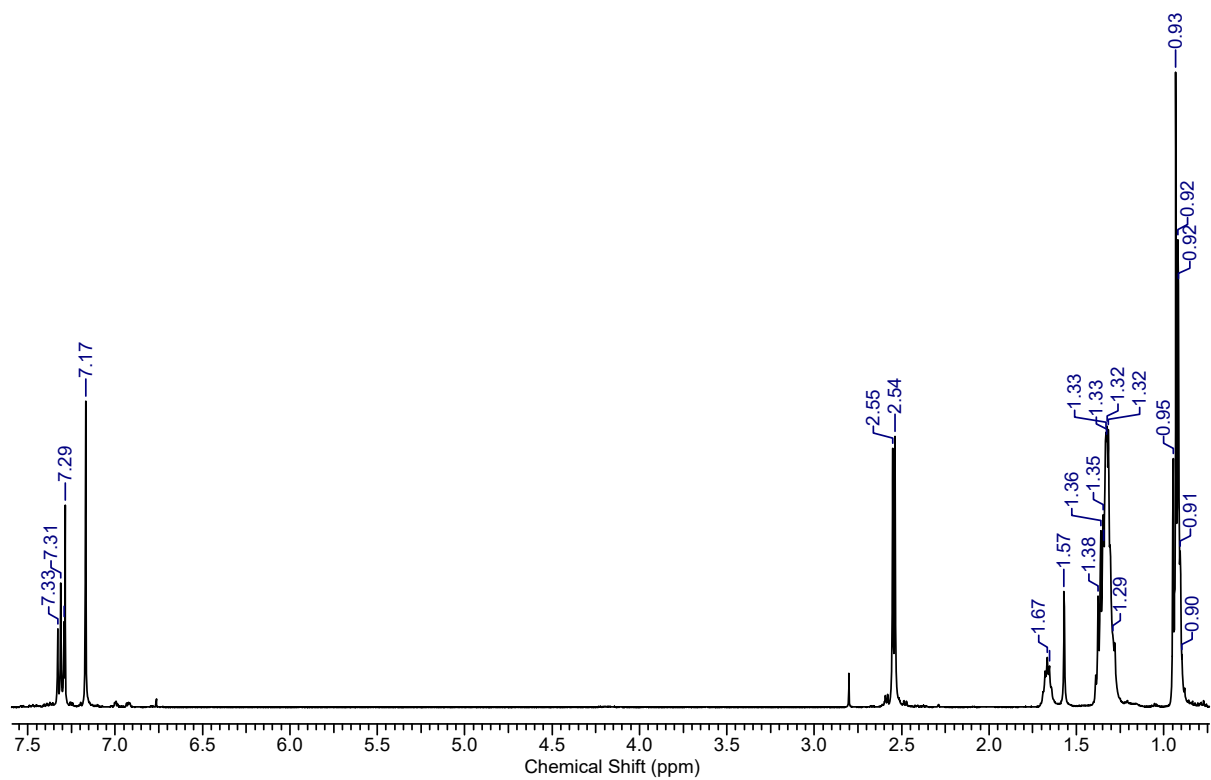


Figure S9. ^1H NMR spectrum of compound TPh-fft.

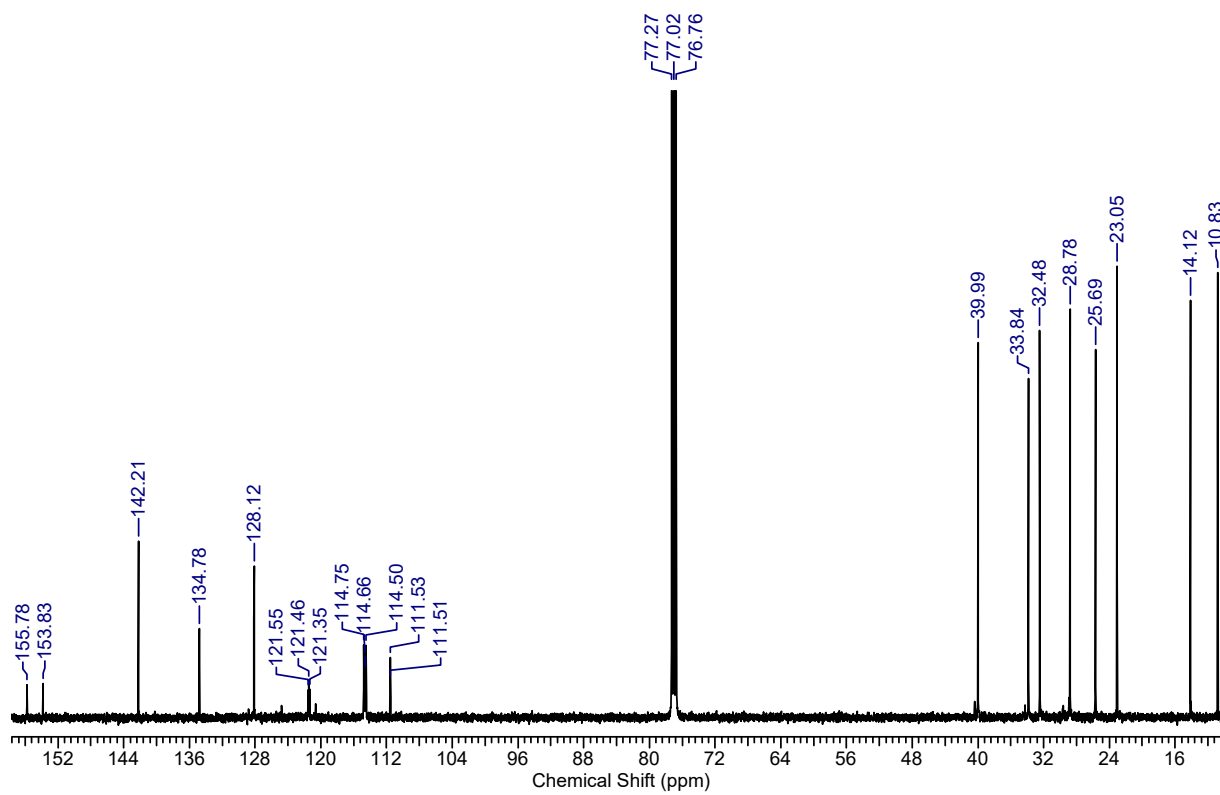


Figure S10. ^{13}C NMR spectrum of compound TPh-fft.

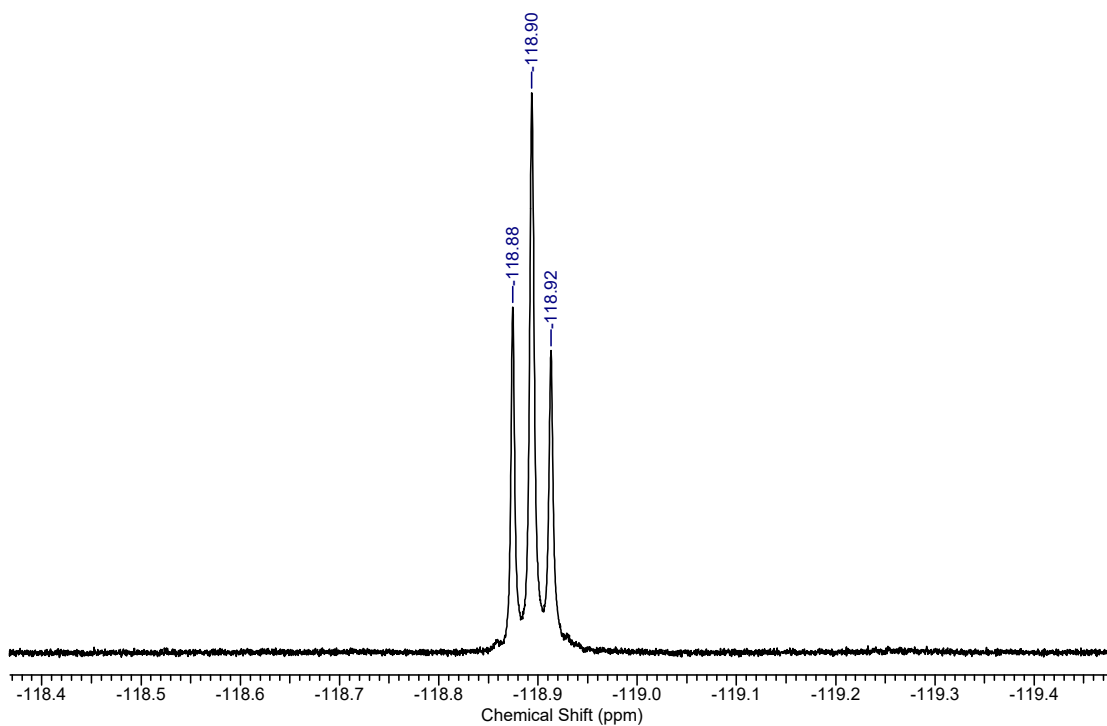


Figure S11. ^{19}F NMR spectrum of compound **TPh-fft**.

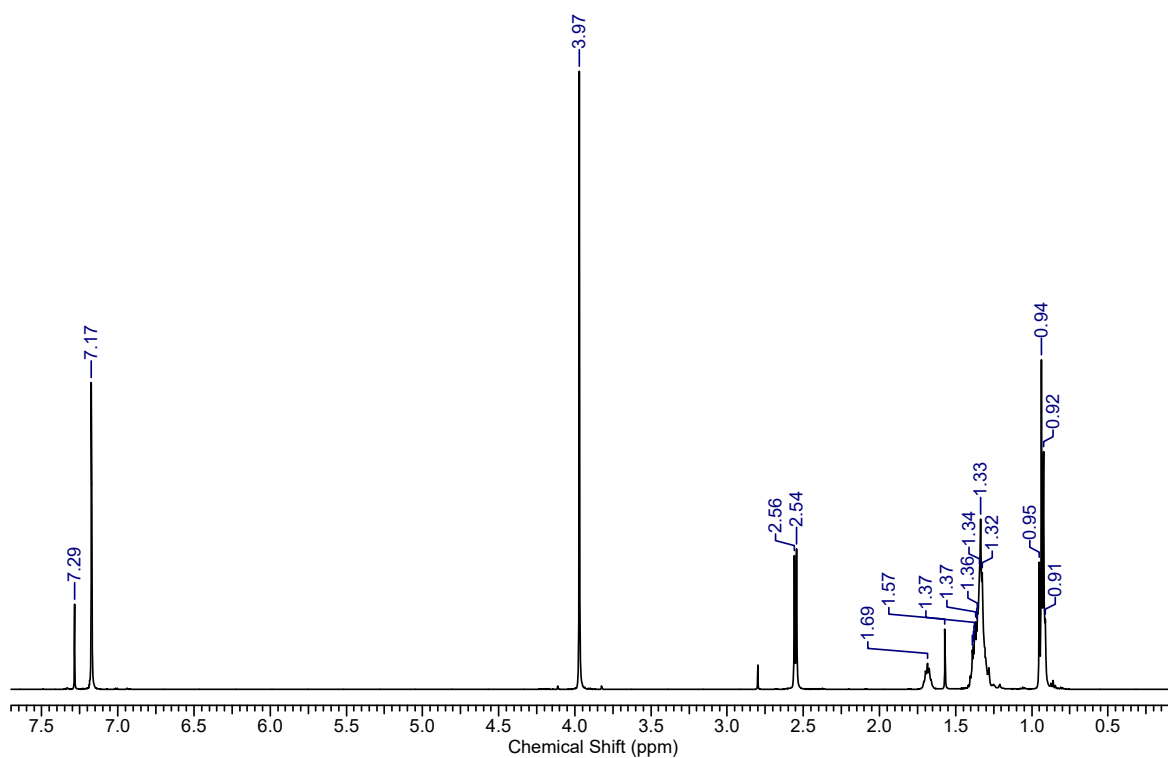


Figure S12. ^1H NMR spectrum of compound **TPh-mmT**.

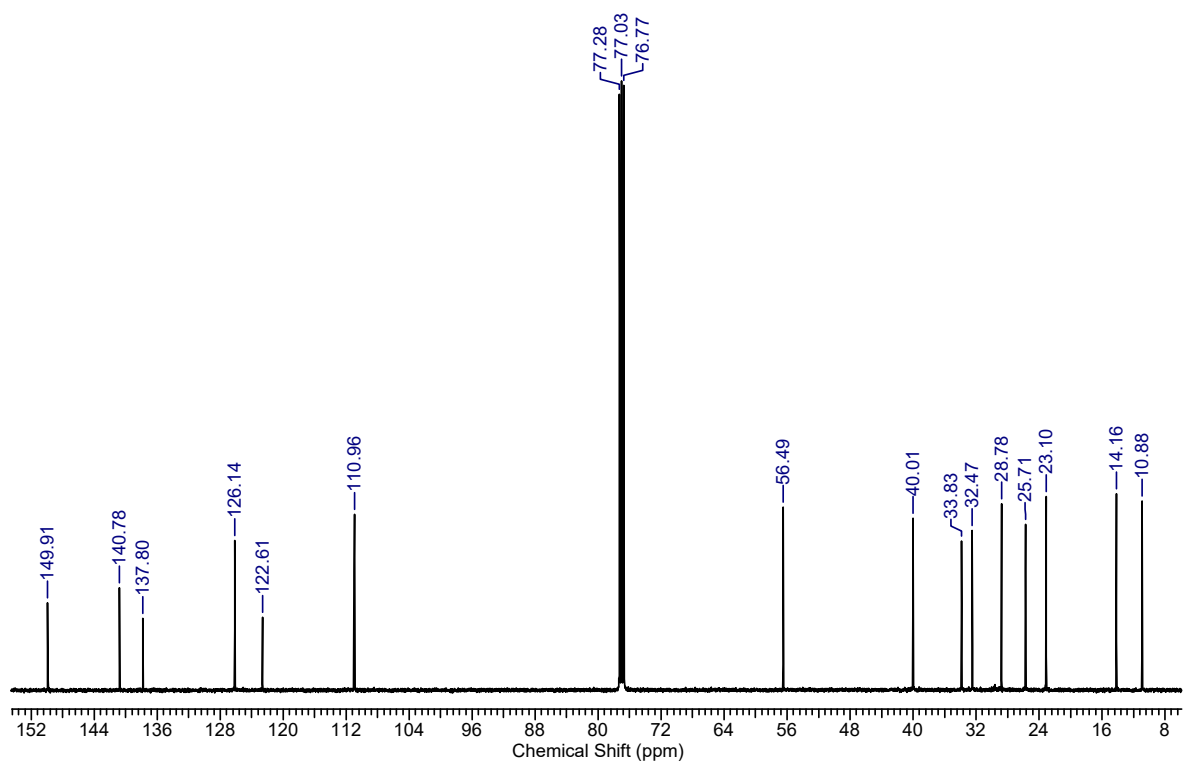


Figure S13. ^{13}C NMR spectrum of compound **TPh-mmT**.

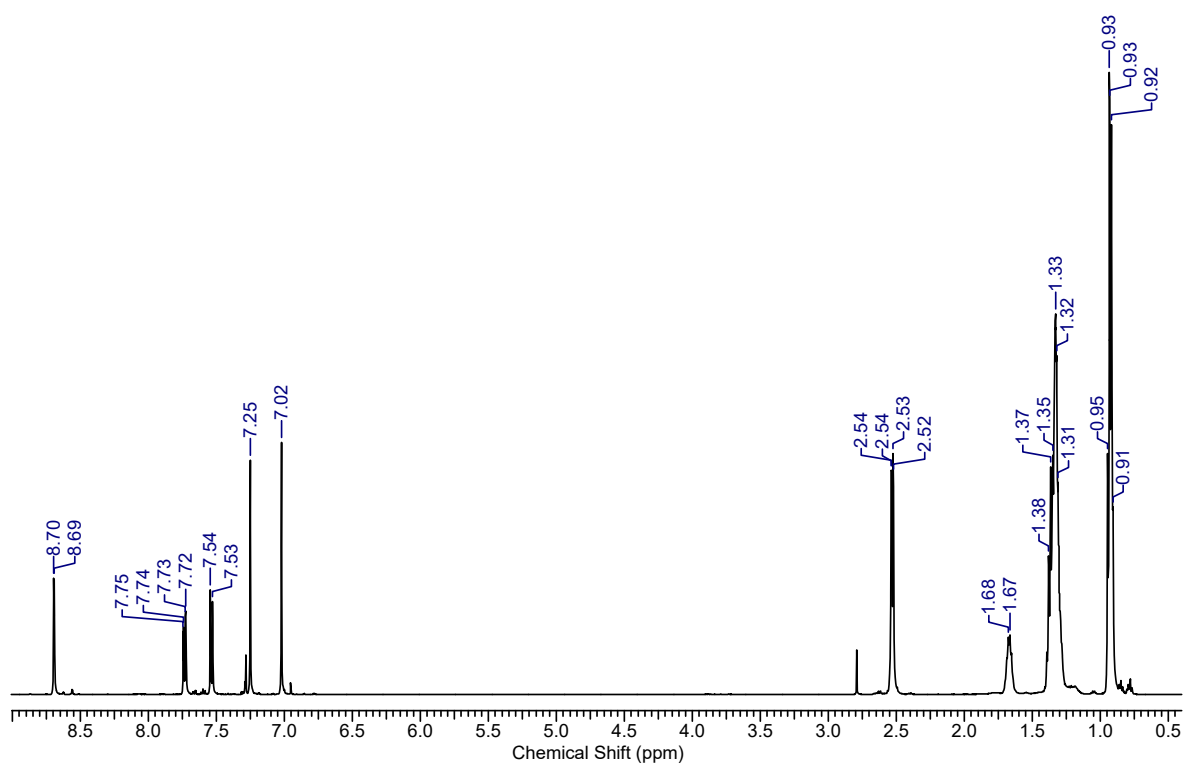


Figure S14. ^1H NMR spectrum of compound **TPyT**.

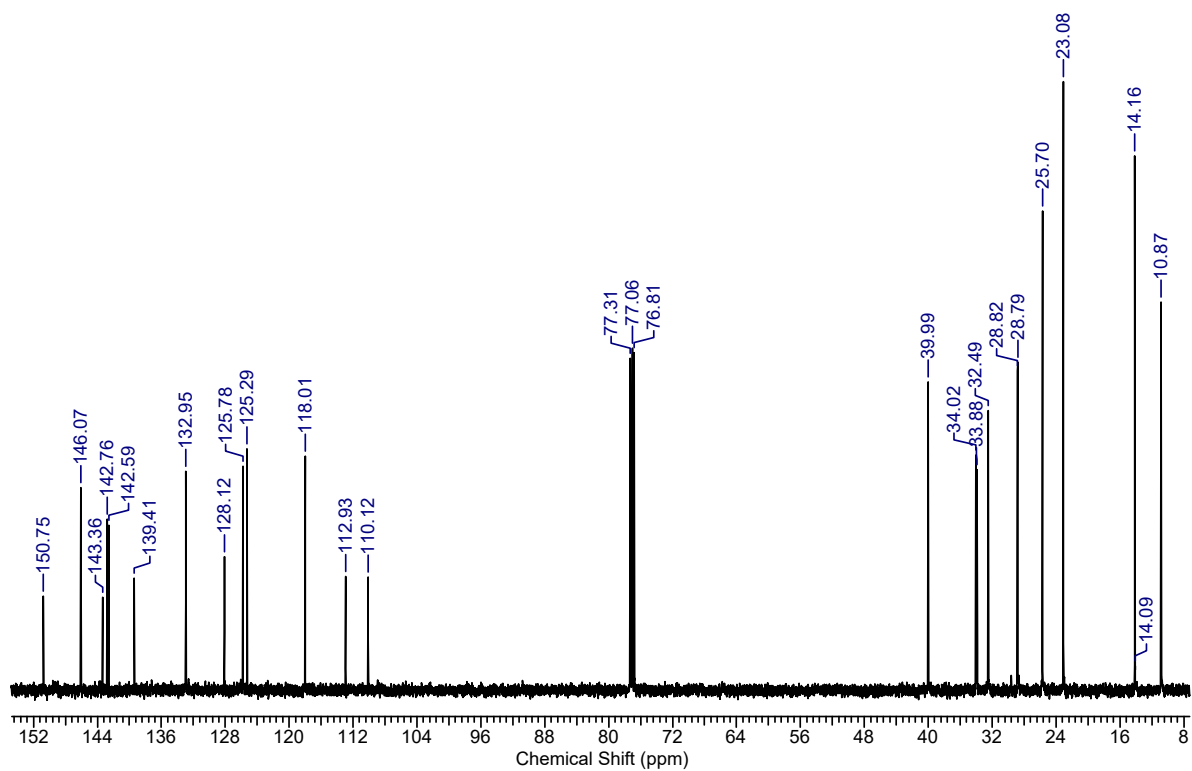


Figure S15. ^{13}C NMR spectrum of compound TPYT.

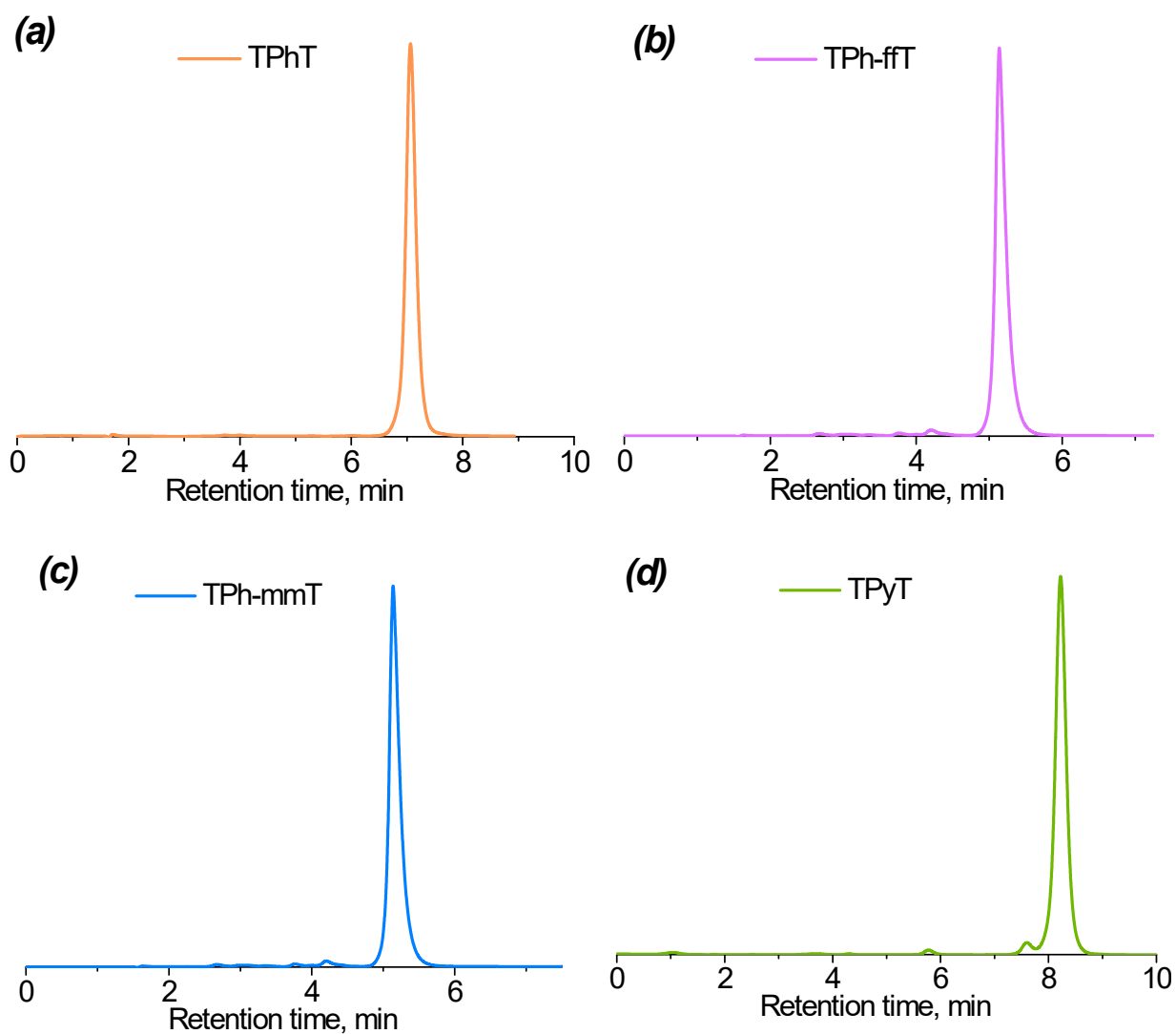


Figure S16. HPLC chromatograms of **TPhT** (a), **TPh-ffT** (b), **TPh-mmT** (c) and **TPyT** (d) monomers. Conditions: eluent - acetonitrile:toluene (7:3); flow rate 1 mL/min; temperature 40°C; column – YMC-C18, 4 μ m, 80Å (4.6 \times 150 mm), detector wavelength 290 nm.

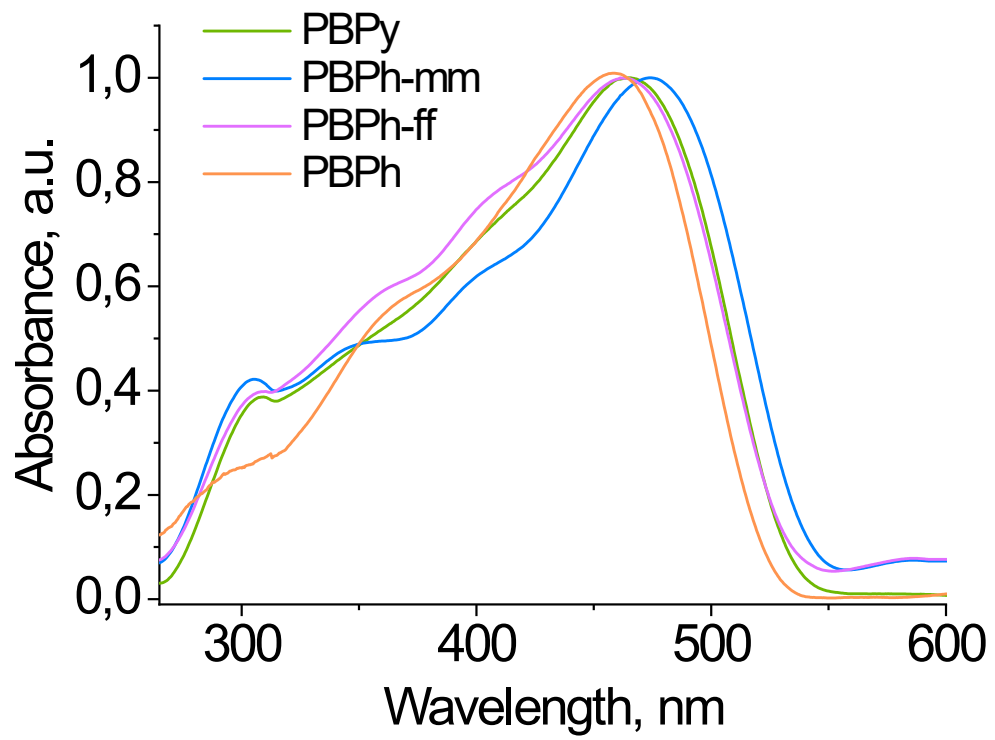


Figure S17. Absorption spectra of polymers in chlorobenzene solution.

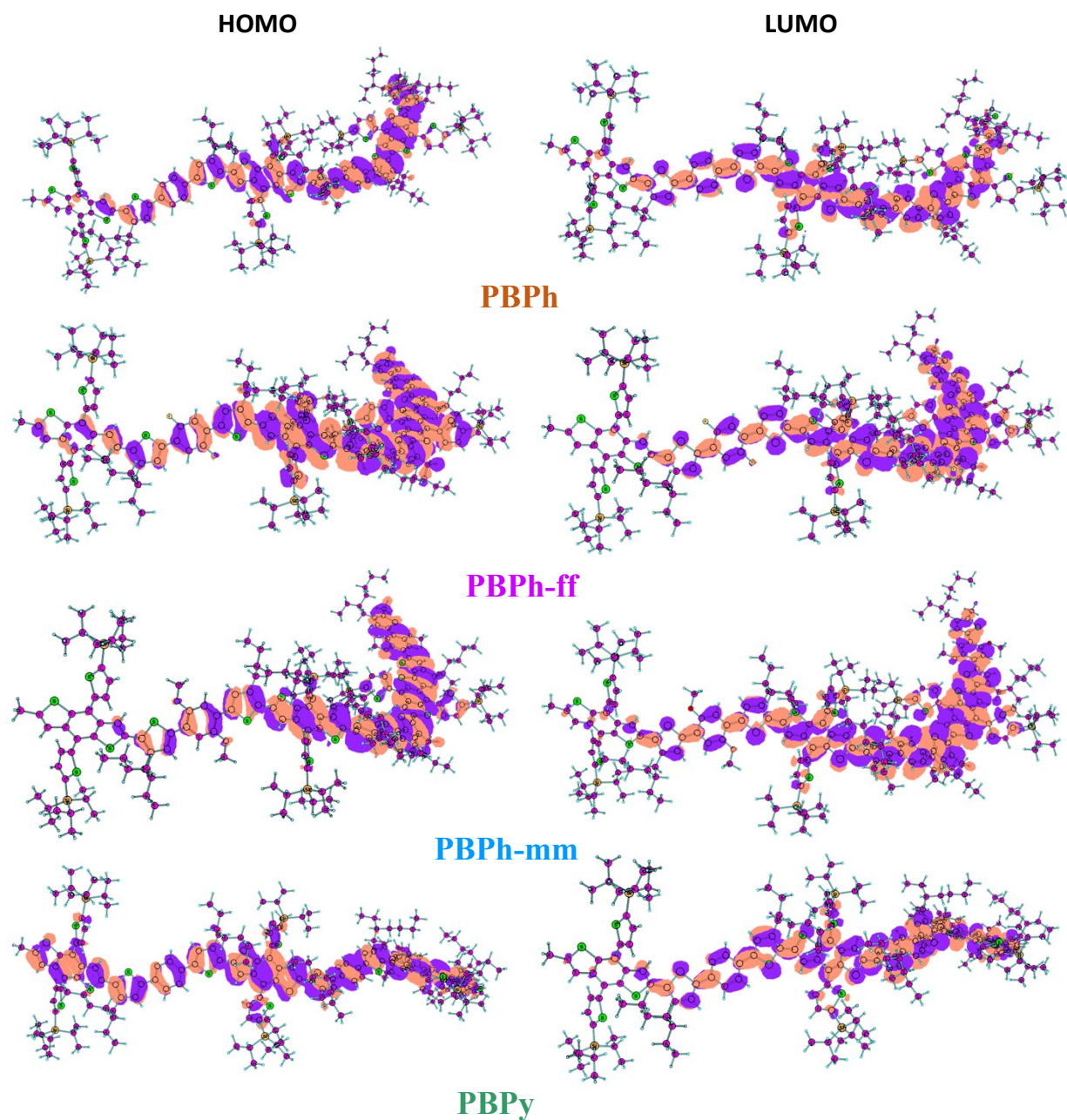


Figure S18. Calculated HOMO and LUMO orbitals of conjugated polymers.

Table S1. HOMO/LUMO energies E (eV) and energy gaps E_g (eV) for trimers calculated using B3LYP/6-31+G(d) approaches in comparison with experimental data.

	experiment			B3LYP/6-31+g*		
	HOMO, eV	LUMO, eV	E_g , eV	HOMO, eV	LUMO, eV	E_g , eV
PBPh	-5.38	-3.11	2.27	-4.949	-2.383	2.566
PBPh-ff	-5.54	-3.29	2.25	-5.001	-2.567	2.434
PBPh-mm	-5.16	-2.98	2.18	-4.701	-2.304	2.396
PBPy	-5.46	-3.18	2.28	-5.028	-2.475	2.553

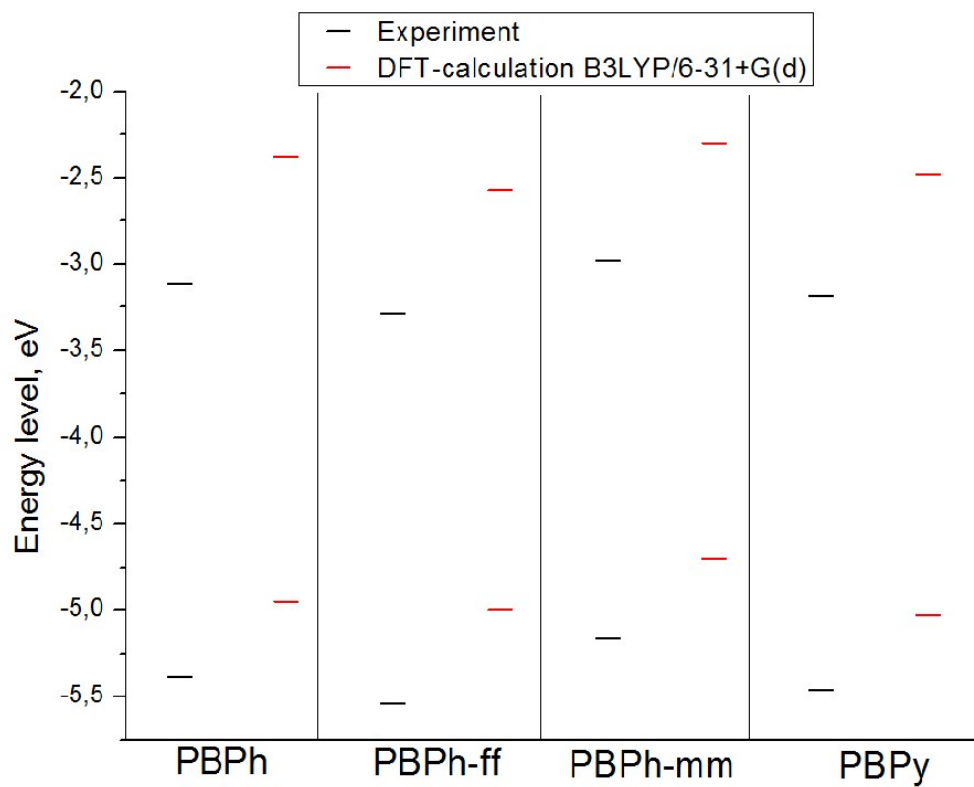


Figure S19. The frontier molecular orbital energy levels as estimated from experimental and predicted by B3LYP/6-31+G(d) calculations.

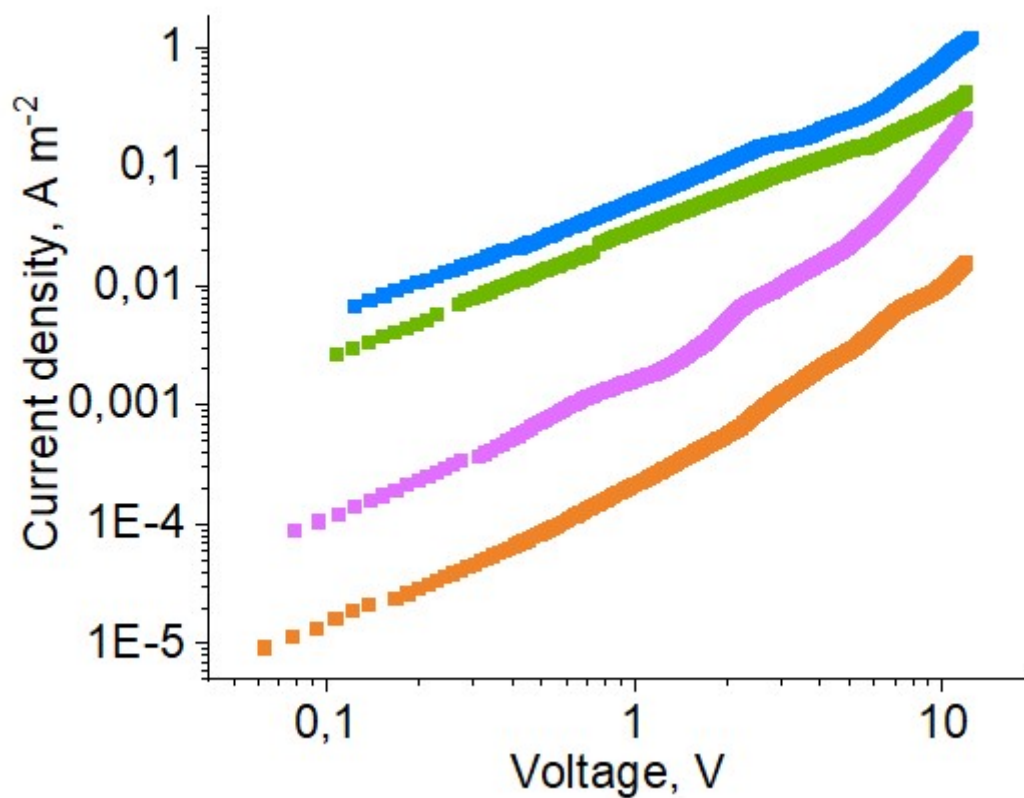


Figure S20. *J-V* curves of hole-only devices based on developed HTMs.

Table S2. Fitted parameters of TRPL decay curves of perovskite with/without HTMs

	A_1	τ_1 , ns	A_2	τ_2 , ns	τ_{ave} , ns
MAPbI ₃	191	4	22	34	18.80
MAPbI ₃ /PBPh	183	3	35	33	23.30
MAPbI ₃ /PBPh-ff	1000	0.5	50	6.3	2.74
MAPbI ₃ /PBPh-mm	320	9	8.4	0.7	8.98
MAPbI ₃ /PBPy	255	5	58	55	40.70

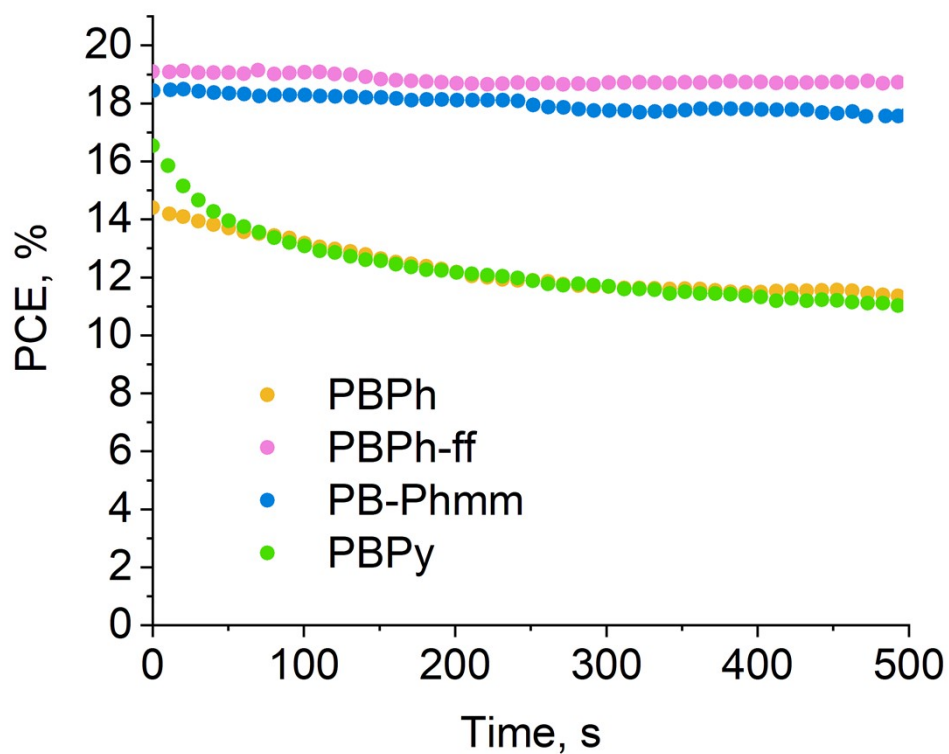


Figure S21. Stabilized power output at the maximum power point under AM 1.5G irradiation.

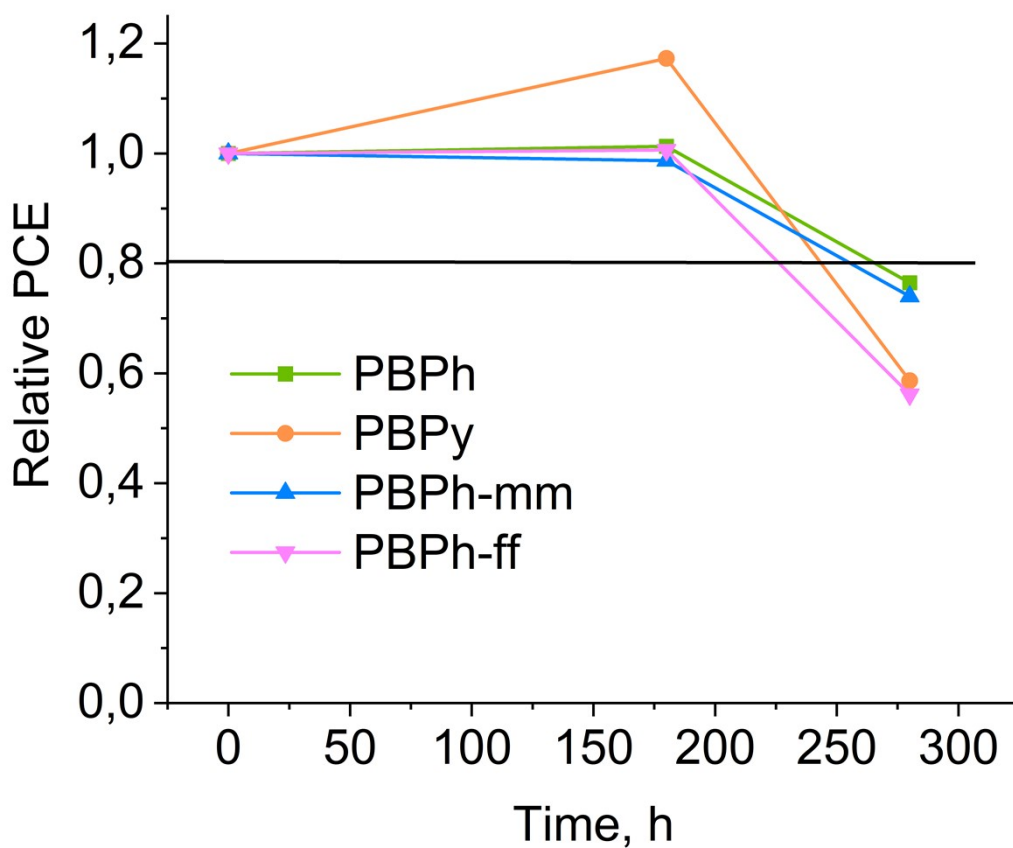


Figure S22. Evolution of relative power conversion efficiency of perovskite solar cells incorporating designed HTMs

References

- 1 I. E. Kuznetsov, A. A. Piryazev, A. F. Akhkiamova, M. E. Sideltsev, D. V. Anokhin, A. V. Lolaeva, M. V. Gapanovich, D. S. Zamoretskov, D. K. Sagdullina, M. V. Klyuev, D. A. Ivanov and A. V. Akkuratov, *ChemPhysChem*, 2023, e202300310.
- 2 A. N. Mikheeva, I. E. Kuznetsov, M. M. Tepliakova, A. Elakshar, M. V. Gapanovich, Y. G. Gladush, E. O. Perepelitsina, M. E. Sideltsev, A. F. Akhkiamova, A. A. Piryazev, A. G. Nasibulin and A. V. Akkuratov, *Molecules*, 2022, **27**, 8333.
- 3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 4 W. J. Stevens, H. Basch and M. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026–6033.
- 5 W. J. Stevens, M. Krauss, H. Basch and P. G. Jasien, *Can. J. Chem.*, 1992, **70**, 612–630.
- 6 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151–156.
- 7 D. N. Laikov, *Chem. Phys. Lett.* 2005, **416**, 116–120.
- 8 E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A.D. Daniels, M. C. Strain, O. Farkas, D.K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople - Gaussian, Inc., Wallingford CT, 2004
- 9 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- 10 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.