Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Po Poly(1-halogen-2-phenylacetylenes) Containing Tetraphenylethene Unit: Polymer Synthesis, Unique Emission Behaviours and Application in Explosive Detection

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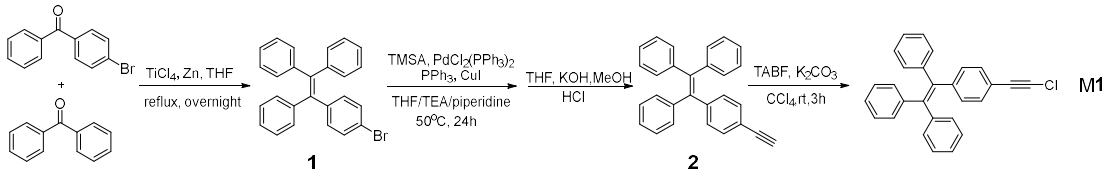
Materials. Unless otherwise noted, all the chemicals were used directly without further purification. Zinc powder was purchased from Shanghai Meixing Chemical Co., Ltd. and picric acid was purchased from Xilong Chemical Co., Ltd., and other reagents were purchased from J&K, Energy, Aladdin, Alfa Aesar, and Macklin. All solvents were purchased from Sinopharm Chemical Reagent Co., Ltd except super dry dichloromethane were purchased from J&K. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium, benzophenone under nitrogen and normal pressure. Triethylamine (Et_3N) was distilled from calcium hydride and dried over potassium hydroxide before use.

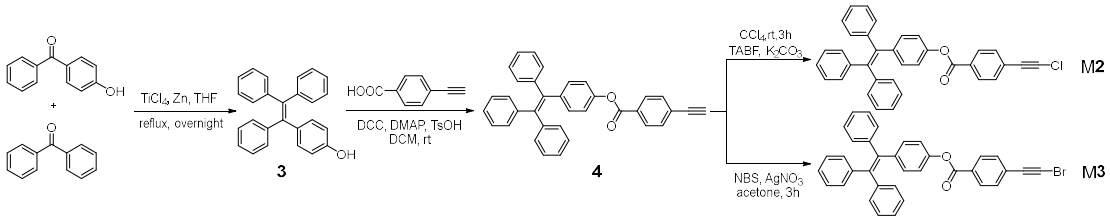
Instrument. Thin-layer chromatography (TLC) analysis was performed by illumination with a UV lamp (254 nm). The molecular weight (M_w and M_n) and polydispersity (M_w/M_n) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system by using a set of monodisperse polystyrene standards covering the molecular weight varying from 10^3 to 10^7 as calibration. FTIR spectra were recorded on a Bruker VECTOR 22 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 spectrometers using $CDCl_3$, DMSO-d_6 or CD_2Cl_2 as solvent. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer in MALDI-TOF mode. UV−visible absorption spectra were measured with a Shimadzu UV-1800 Spectrophotometer and PL spectra were measured with an RF-5301 PC spectrofluorometer. Single crystal X-ray diffraction analysis was conducted on a Gemini A Ultra diffractometer at 293 K.

Monomer Preparation. The intermediate reagent **1**, **2**, **3**, **4** were obtained by the early reported procedure, and three monomers M**1**, M**2**, M**3** were prepared by optimizing synthetic routes of literatures[1-5]. The synthetic routes to monomers are shown in Schemes S1 and S2 and the detailed synthetic procedures are shown below.

Scheme S1. Synthetic route to M**1**.



Scheme S2. Synthetic route to M**2** and M**3**.



1-(4-Bromophenyl)-1,2,2-triphenylethene (1) A previously reported procedure[4] was used to synthesize this compound with white solid in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 6.88-6.90 (m, 2H), 7.13-6.89 (m, 17H).

1-(4-(2-Ethynyl)phenyl)-1,2,2-triphenylethene (2) A previously reported procedure[2] was used to synthesize this compound with white solid in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 7.23-7.21 (m, 2H), 7.11-7.09 (m, 9H), 7.04-6.99 (m, 8H), 3.03 (s, 1H).

4-(1,2,2-Triphenylvinyl)phenol (3) 4-(1,2,2-Triphenylvinyl)phenol was synthesized according previously reported procedure[1] with the white solid in 33% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm) 9.36 (s, 1H), 7.19-6.92 (m, 15H), 6.74 (d, 2H, J = 6.74 Hz), 6.50 (d, 2H, J = 6.50 Hz).

Tetraphenyl vinyl methoxycarbonyl phenyl acetylene (4) 4-Carboxyphenylacetylene (0.73g, 5 mmol), intermediate reagent **3** (1.74 g, 5 mmol), DCC (1.50 g, 7.25 mmol), DMAP (122.17 mg, 1 mmol) and TsOH (190.20 mg, 1 mmol) were placed into a 250 mL round-bottom flask with 150 mL THF. The resultant mixture was stirred at room temperature nearly 24 h (monitored by TLC). The filtrate was concentrated by a rotary evaporator after filtering the urea salts and wash with diethyl ether three times. The result product was purified column chromatography (SiO_2, PE/DCM, 1:4, v/v) to give a white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 8.11 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.14-7.02 (m, 17H), 6.97-6.95 (m, 2H), 3.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.3, 149.1, 143.6 – 143.4, 141.4, 140.0, 132.4, 132.2, 131.2 – 131.4, 129.9.0, 129.5, 127.8 – 127.6, 127.4, 126.6 – 126.5, 120.7, 82.7, 80.5.

1-Chloro-2-tetraphenyl vinyl acetylene (M1) Potassium carbonate (691.05 mg, 5 mmol) and intermediate reagent **2** (1.78 g, 5 mmol) was fed into a 100 mL two-necked flask and purge the under high purity N_2. CCl_4 (50 mL) and tetrabutylammonium fluoride (TBAF, 1

M in THF, 3 mL, 3 mmol) was added and stirred at 35 ºC for 3h. The result mixture was filtrated and extracted by dichloromethane for three times. The organic layer was evaporated after washing with brine and water and drying over Na_2SO_4. The residue was purified by column chromatography (SiO_2, PE/DCM, 4:1, v/v) to give a light orange solid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 7.16 (m, 2H), 7.12-7.08 (m, 9H), 7.01-7.00 (m, 6H), 6.97 – 6.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.3, 143.7, 143.4-143.2, 141.8, 140.9, 140.1, 131.5-131.3, 127.9 -127.6, 126.7-126.4, 119.9, 69.5, 68.0. IR (KBr), *v* (cm^{-1}): 2214 (C≡C stretching). HRMS (TOF-MS): calcd. for $C_{28}H_{19}Cl$ 390.1175, found 390.1176.

1-Chloro-2-benzoic acid tetraphenyl vinyl ester acetylene (M2) As a general procedure, intermediate reagent **4** (2.38 g, 5 mmol), NCS (1.00 g, 7.5 mmol) and $AgNO_3$ (84.90 mg, 0.5 mmol) and TBAF (1 M in THF, 3 mL, 3 mmol) were dissolved in acetonitrile (50 mL) and the mixture was stirred at 35 °C for 3 h. Then the mixture was filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA, 10:1, v/v)) to give a white solid in 85% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ (TMS, ppm) 8.09 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.02 (m, 17H), 6.96 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 164.7, 149.7, 144.0-143.9, 141.9, 140.4, 132.6, 132.5, 131.6-131.5, 130.3, 129.8, 128.2-128.0, 127.7, 127.0-126.9, 121.2, 71.9, 69.9. IR (KBr), *v* (cm^{-1}): 2200 (C≡C stretching), 1740(C=O stretching). HRMS (ESI): calcd. for $[C_{35}H_{23}O_2Cl+H]^+$ 511.1459, found 511.1428

1-Bromo-2-benzoic acid tetraphenyl vinyl ester acetylene (M3) The synthetic procedures of M**3** are similar with that of M**2**. Intermediate reagent **4** (2.38 g, 5 mmol), NBS (1.42 g, 7.5 mmol) and $AgNO_3$ (84.90 mg, 0.5 mmol) were dissolved in acetone (50 mL) and the mixture was stirred at room temperature for 3 h. Then the mixture was filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA, 10:1, v/v)) to give a white solid in 87% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ (TMS, ppm) 8.09 (d, *J* = 10.1 Hz, 2H), 7.57 (d, *J* = 10.1 Hz, 2H), 7.16 – 7.03 (m, 17H), 6.97 – 6.95 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 164.6, 149.6, 144.0-143.9, 141.9, 140.4, 132.6-132.5, 131.6-131.5, 130.3-129.9, 128.2-128.0, 127.0-126.9, 121.2, 79.6, 27.3. IR (KBr), *v* (cm^{-1}): 2200 (C≡C stretching), 1740(C=O stretching). HRMS (ESI): calcd. for $[C_{35}H_{23}O_2Br+Na]^+$ 577.0774, found 577.0771.

Polymerization. The polymerization reaction was carried out under dry nitrogen by using the standard glovebox or Schlenk technique except for polymer purification. The catalysts and co-catalysts were stirred in the desired solvent at the desired temperature for 20 min. After the solution of monomer addition, the mixture was stirred at a pre-set temperature for desired time and the reaction was quenched with nearly 8-10 mL methanol. The resulting polymer was precipitated in nearly 100 mL methanol and wash three times by methanol before filtered and dried under vacuum.

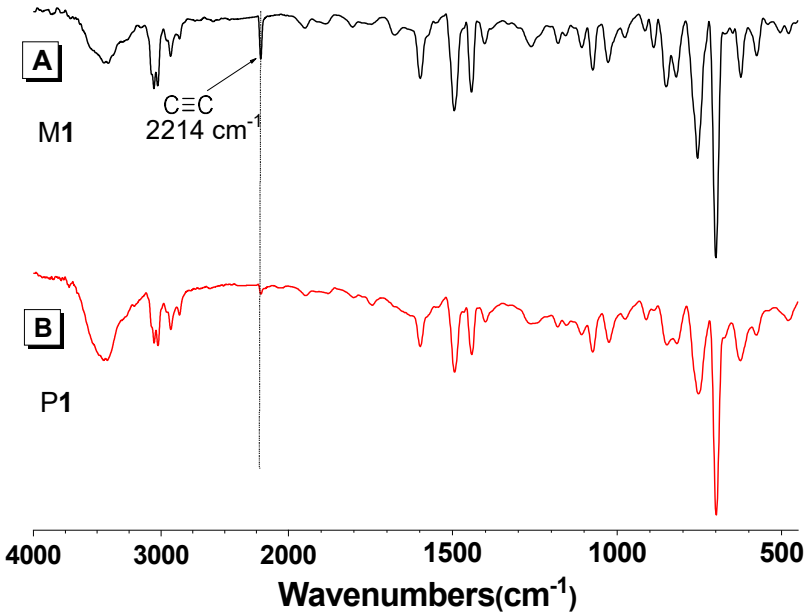


Figure S1. FTIR spectra of (A) M**1**, (B) P**1** in KBr pellets.

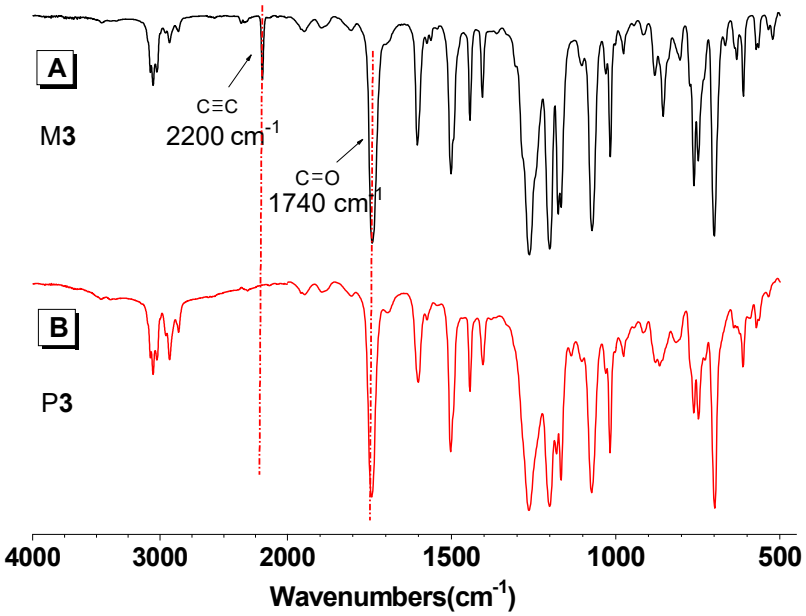


Figure S2. FTIR spectra of (A) M**3**, (B) P**3** in KBr pellets.

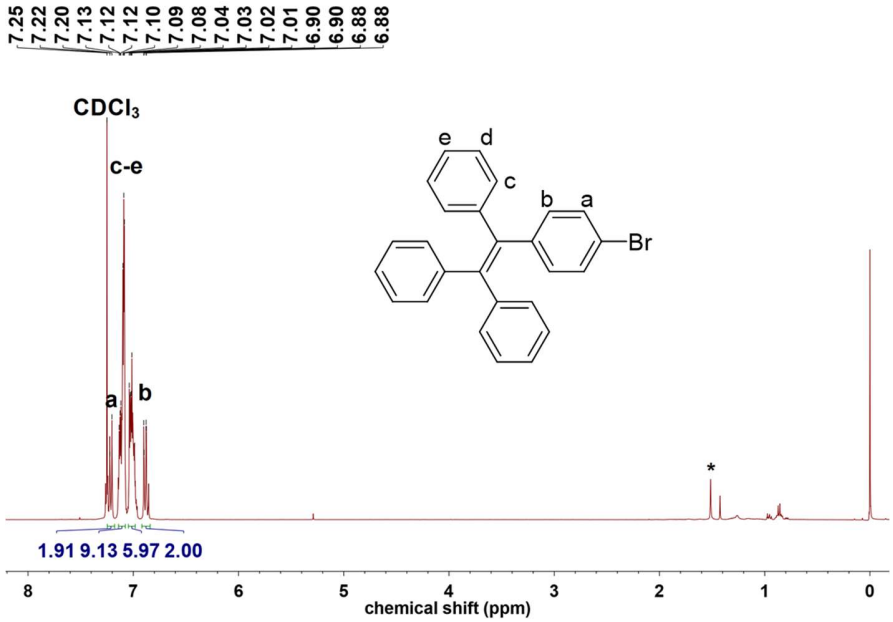


Figure S3. ^{1}H NMR spectrum of **1** in $CDCl_3$. The solvent peaks are marked with asterisks.

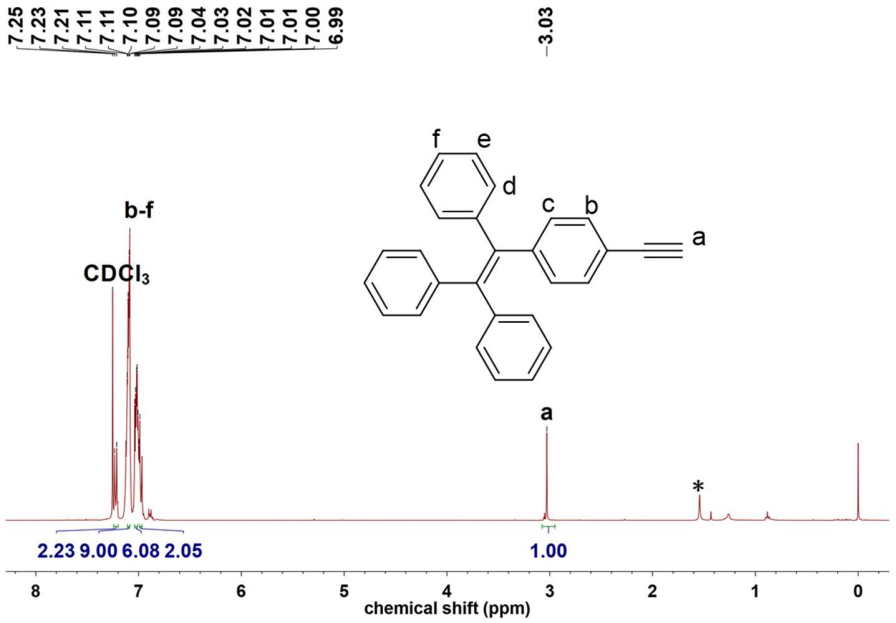


Figure S4. ^{1}H NMR spectrum of **2** in $CDCl_3$. The solvent peaks are marked with asterisks.

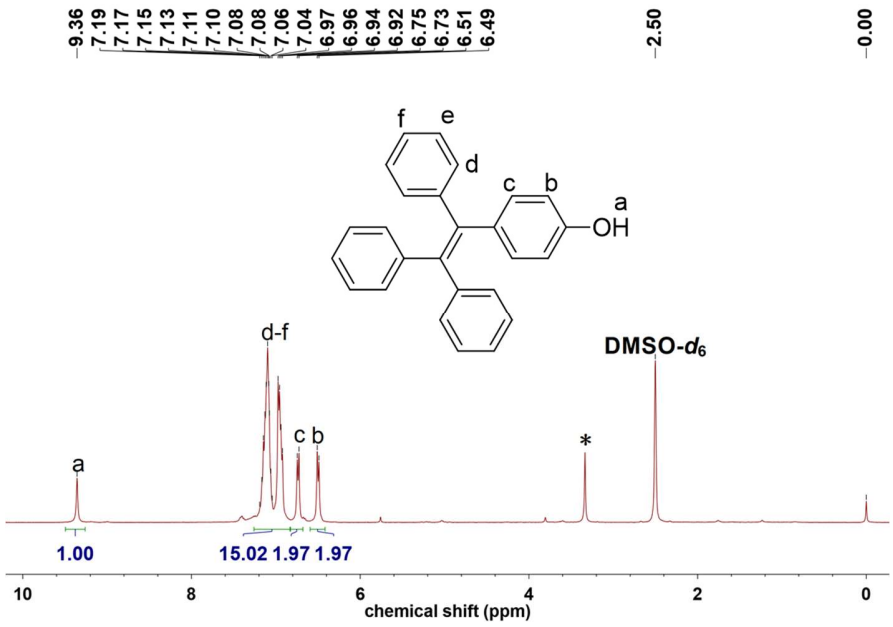


Figure S5. ^{1}H NMR spectrum of **3** in DMSO-d_6. The solvent peaks are marked with asterisks.

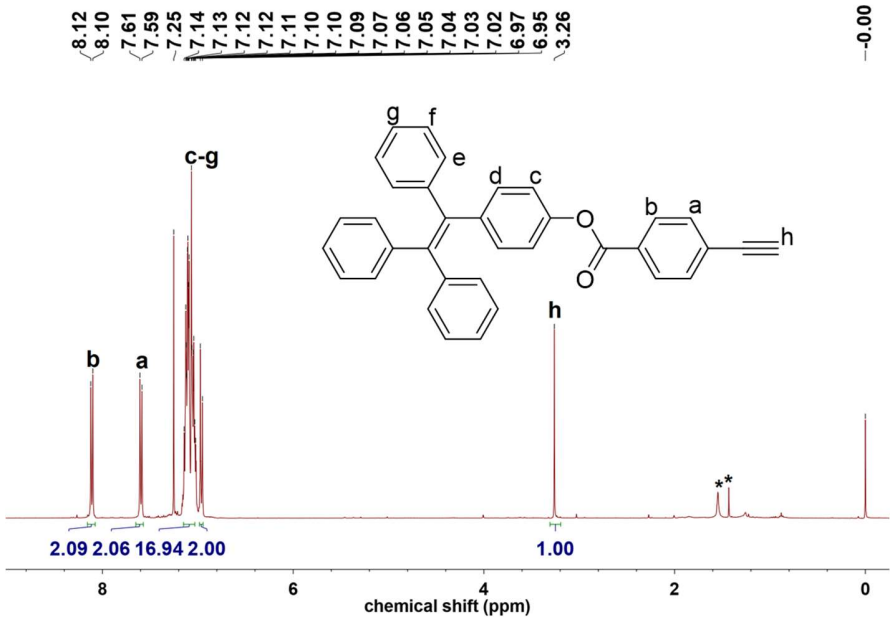


Figure S6. ^{1}H NMR spectrum of **4** in $CDCl_3$. The solvent peaks are marked with asterisks.

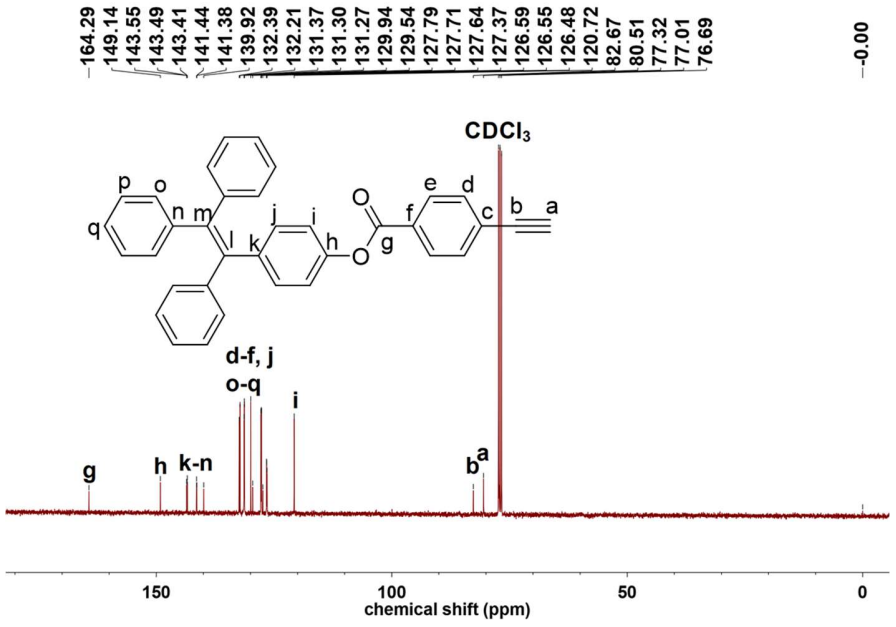


Figure S7. ^{13}C NMR spectrum of **4** in $CDCl_3$.

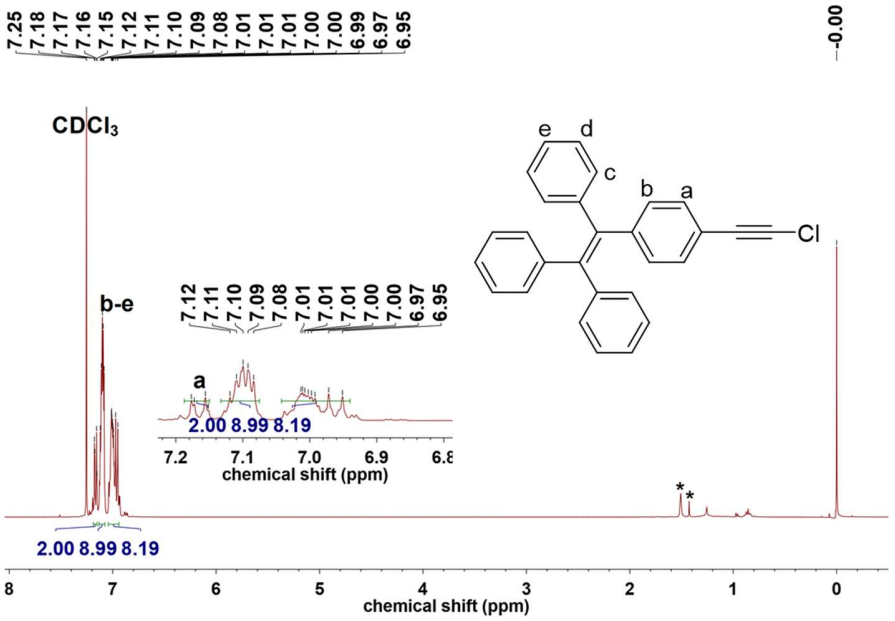


Figure S8. ^{1}H NMR spectrum of M**1** in $CDCl_3$. The solvent peaks are marked with asterisks.

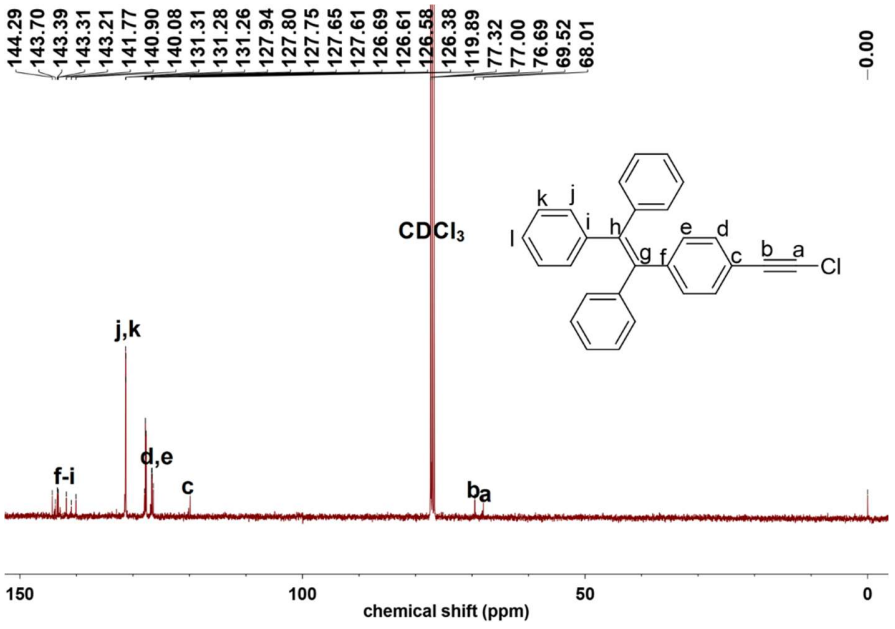


Figure S9. ^{13}C NMR spectrum of M**1** in $CDCl_3$.

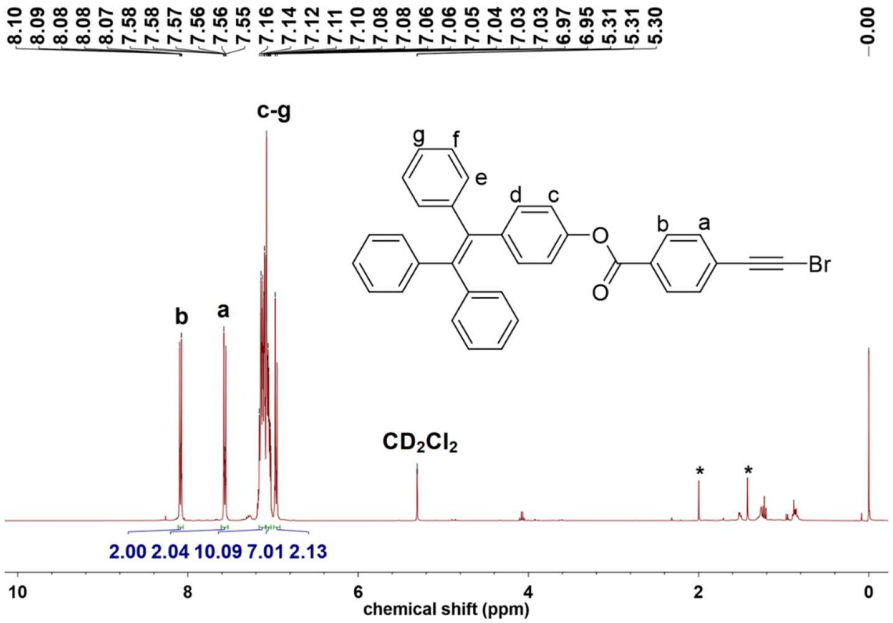


Figure S10. ^{1}H NMR spectrum of M**3** in CD_2Cl_2. The solvent peaks are marked with asterisks.

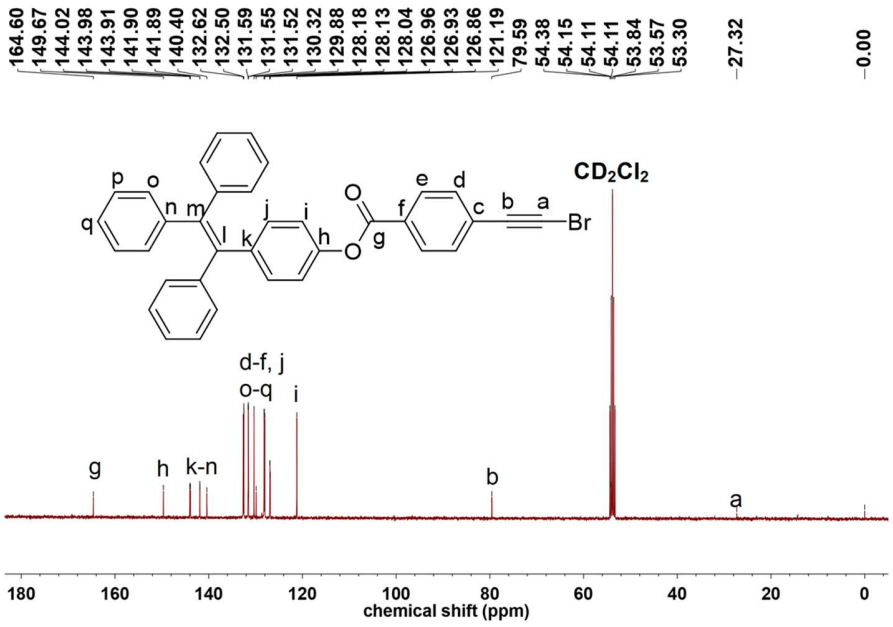


Figure S11. ^{13}C NMR spectrum of M**3** in CD_2Cl_2.

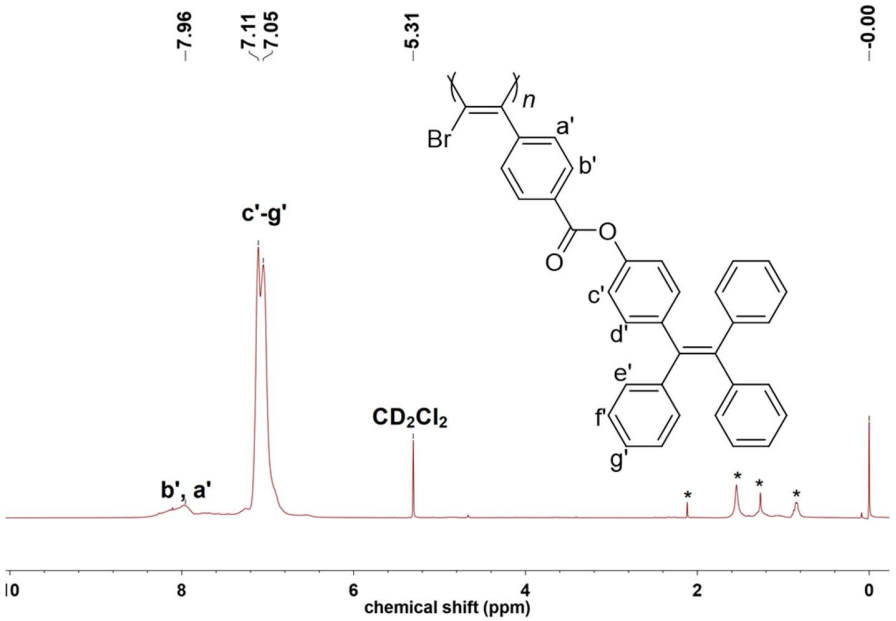


Figure S12. ^{1}H NMR spectrum of P**3** in CD_2Cl_2. The solvent peaks are marked with asterisks.

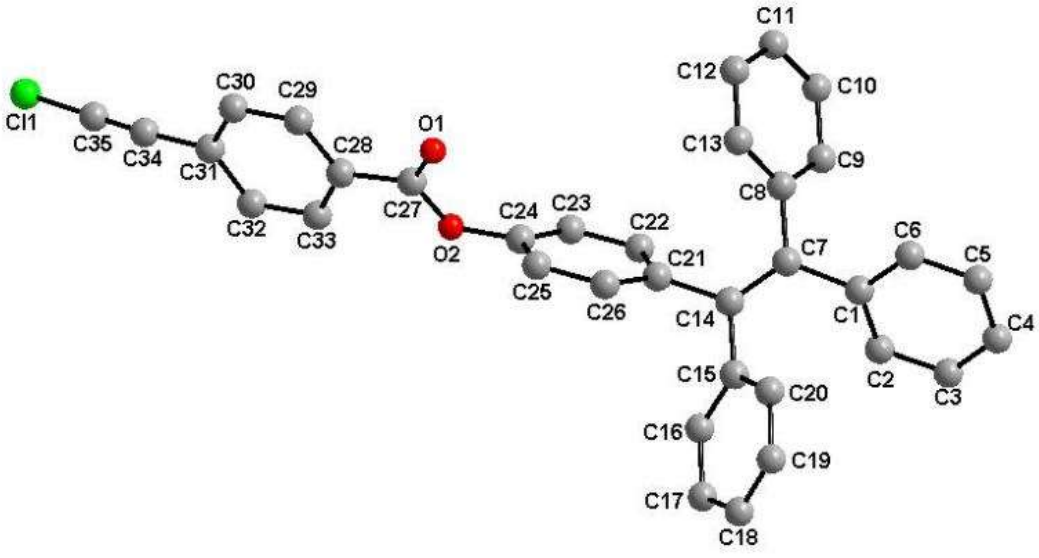


Figure S13. Crystal structure of compound M**2** (hydrogen atoms are omitted for clarity).

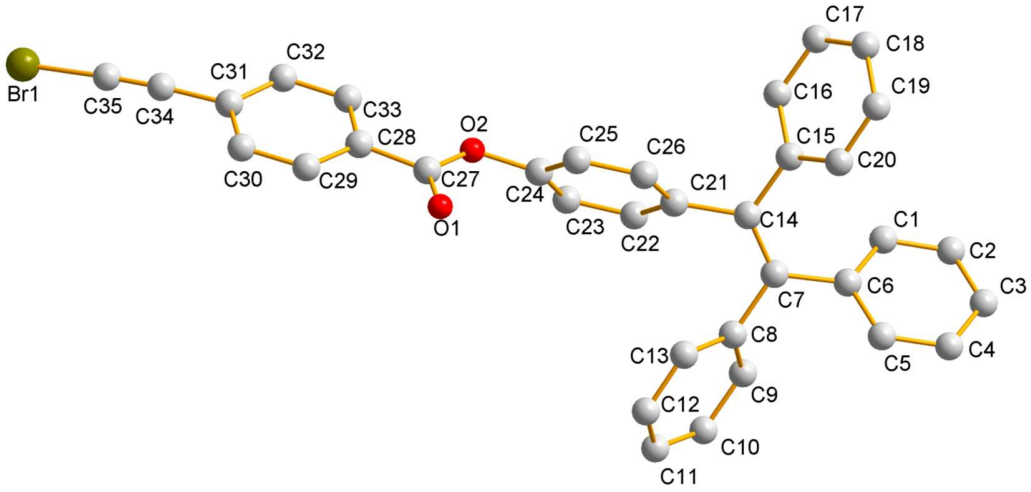


Figure S14. Crystal structure of compound M**3** (hydrogen atoms are omitted for clarity).

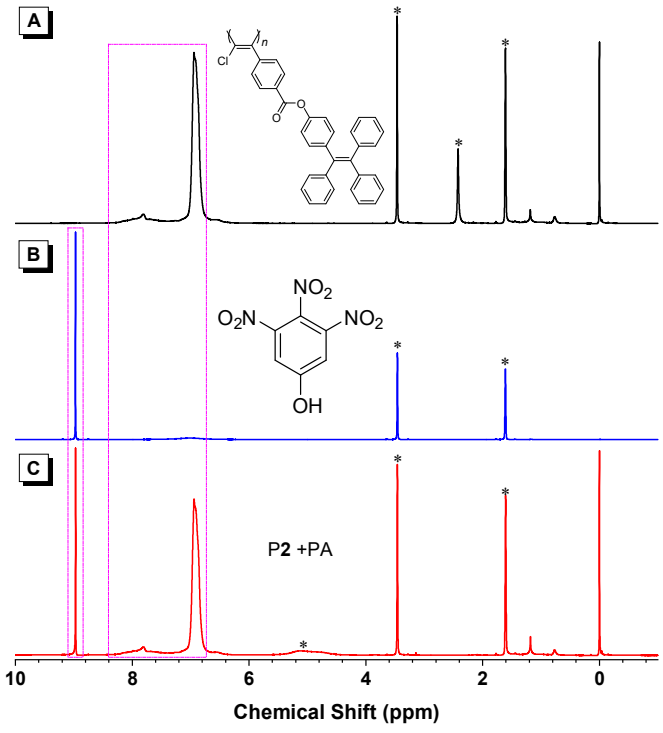


Figure S15. ^{1}H NMR spectra of P**2** (A) PA (B) and the mixture of PA and P**2** (C) in THF-d_8. The solvent peaks are marked with asterisks.

Table S1. Crystallographic data and the structure refinement for compounds M**2** and M**3**.

Compound	**M2**	**M3**
CCDC number	1938578	2073602
Empirical fomula	$C_{35}H_{23}ClO_2$	$C_{35}H_{23}BrO_2$
Fomula weight (g·mol-1)	510.98	555.44
Temperature(K)	170	170
Wavelength(A)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P 1 21/c 1	P 1 21/c 1
a (Å)	12.0595(3)	12.175(7)
b (Å)	11.2560(3)	11.191(8)
c (Å)	20.0268(5)	20.212(13)
α (°)	90	82.8560(10)
β (°)	99.789(1)	98.916(19)
γ (°)	90	81.7690(10)
Volume($Å^3$)	2678.89(12)	2720.62(300)
Z, Calculated density($g·cm^{-3}$)	4	4
Dcalc (g·cm-3)	1.267	1.356
Absorption coefficient (mm-1)	0.173	1.541
F(000)	1064.0	1136.0
Theta max for data collection	26.374	27.056
Limiting indices	-15 ≤h ≤15 -14 ≤h ≤14 -25 ≤h ≤25	-15 ≤h ≤15 -14 ≤h ≤14 -25 ≤h ≤25
Reflections collected/unique	4448/5416	4183/5930
Data completeness	0.990	0.994
Max. and min. transmision	0.690,0.745	0.667,0.746
Data/parameters Rindices(all data)	0.0503, 0.1463	0.0467, 0.1358
S	1.029	1.053

Table S2. Particle size distributions of solution of P**2** with different concentration.

Sample Concentration (M)	Number Mean (d.nm)	PDI
10^{-5}	9	0.25
$7*10^{-5}$	7	0.36
10^{-4}	20	0.31
$2*10^{-4}$	24	0.37
$3*10^{-4}$	30	0.37
$7*10^{-4}$	32	0.28
10^{-3}	43	0.36

References:

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3 W. Z. Yuan, J. Z. Sun, Y. Dong, M. Häussler, F. Yang, H. P. Xu, A. Qin, J. W. Y. Lam, Q. Zheng and B. Z. Tang, Wrapping carbon nanotubes in pyrene-containing poly(phenylacetylene) chains: solubility, stability, light emission, and surface photovoltaic properties, *Macromolecules*, 2006, **39**, 8011.

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