Facile synthesis of functional poly(vinylene sulfide)s containing donor-acceptor chromophores by double click reaction

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Supporting Information

Experimental

General Measurements

^{1}H-NMR spectra were measured on a BRUKER AVANCE III HD NMR spectrometer (500 MHz) at 20 ℃. Chemical shifts are reported in parts per million downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), m (multiplet) and br (broad). FT-IR was recorded on a Perkin-Elmer LR-64912C Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) was measured on a Shodex system equipped with polystyrene gel columns using THF as an eluent at a flow rate of 1.0 mL·min^{-1}. Relative molecular weights were determined by comparison with the calibrated standard polystyrenes. Thermo gravimetric analysis (TGA) were carried out on a STA 449 F3 Jupiter, and the differential scanning calorimetry (DSC) measurements were carried out on a Perkin Elmer Pyris 6 DSC, under nitrogen flow at a scanning rate of 10 ℃·min^{-1}. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating potential of 20 kV by a linear positive ion mode with dithranol as a matrix. Elemental analyses were performed at institute of chemistry Chinese academy of sciences, with a Flash EA 1112 instrument. UV-vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Glassy Carbon working electrodes of 2 mm diameter, a platinum wire counter

electrode, and an Ag/Ag$^+$/CH$_3$CN/Bu$_4$NPF$_6$ reference electrode on a computer-controlled CHI 660C instrument at room temperature (rt). All potentials were referenced to the ferricinium/ferrocene (Fc/Fc$^+$) couple used as an internal standard. The nonlinear optical properties (NLO) response was measured by means of Z-scan technique, employing 20 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser.

Materials

All reagents were purchased from commercial sources (J&K, Aldrich) and used without further purification.

Compound 1, 2 and M1 were synthesized based on the reference D. Wang, Q. S. Guo, H. Gao, Z. Yang, Y. Xing, H. Cao, W. L. He, H. H. Wang, J. M. Gu and H. Y. Hu, Polym. Chem., 2016, DOI: 10.1039/c6py00106h.

4-((2,5-Dibromophenyl)ethynyl)-N,N-dihexadecylaniline   (1)

To a degassed solution of 4-ethynyl-N,N-diihexylaniline (3.00 g, 5.31 mmol) and 1,4-dibromo-2-iodobenzene (2.30 g, 6.37 mmol) in triethylamine (TEA) (40 mL) and tetrahydrofuran (THF) (40 mL), bis(triphenylphosphine) palladium(II) dichloride (PdCl$_2$(PPh$_3$)$_2$) (0.22 g, 0.32 mmol) and cuprous iodide (CuI) (0.12 g, 0.64 mmol) were added under Ar. The mixture was stirred at 40 ºC for 15 h. After removal of the precipitated salt, evaporation and column chromatography (SiO$_2$, V$_{hexane}$/V$_{dichloromethane(DCM)}$ = 20:1) afforded the desired product (1) (yellowish solid, 2.62 g, 62%). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ = 0.90 (m, 6H), 1.29 (s, 52H), 1.58 (m, 4H), 3.30 (m, 4H), 6.60 (d,J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 1H), 7.65 (s, 1H) ppm. FT-IR (KBr): ν = 2925, 2854, 2203, 2156, 1604, 1550, 1532, 1519, 1466, 1405, 1369, 1249, 1188, 1140, 1097, 1029, 952, 860, 843, 812, 760 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{46}$H$_{73}$Br$_2$N: 799.41 g•mol^{-1}, found: 800.3 g•mol^{-1} [MH]$^+$; elemental analysis calcd (%) for C$_{46}$H$_{73}$Br$_2$N (799.41): C 69.11, H 9.48, N 1.70. found: C 69.10, H 9.49, N 1.69.

4-((2,5-Bis((trimethylsilyl)ethynyl)phenyl)ethynyl)-N,N-dihexadecylaniline (2)

The compound (**1**) (2.00 g, 2.51 mmol) and (triisopropylsilyl)acetylene (TMSA) (0.74 g, 7.53 mmol) was dissolved in TEA/THF ($V_{TEA}:V_{THF}$ = 1:1, 40 mL). After the solution was purged with bubbling Ar for 30 min, $PdCl_2(PPh_3)_2$ (0.11 g, 0.15 mmol) and CuI (0.06 g, 0.30 mmol) were added. The reaction mixture was then stirred at 80 ºC for 12 h under Ar. The mixture was concentrated, rediluted with DCM, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, V_{hexane}/V_{DCM} = 10:1) to give (**2**) (red solid, 1.00 g, 48%). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.27 (m, 18H), 0.89 (m, 6H), 1.28 (m, 52H), 1.58 (m, 4H), 3.29 (m, 4H), 6.58 (d, J = 9.0 Hz, 2H), 7.28 (s, 1H), 7.40 (m, 3H), 7.60 (s, 1H) ppm. FT-IR (KBr): ν = 2916, 2851, 2206, 1604, 1515, 1472, 1402, 1369, 1198, 1122, 1078, 1029, 878, 808, 715 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{56}H_{91}NSi_2$: 833.70 g•mol^{-1}, found: 834.8 g•mol^{-1} [MH]$^+$; elemental analysis calcd (%) for $C_{56}H_{91}NSi_2$ (833.70): C 80.37, H 11.01, N 1.72. found: C 80.34, H 11.03, N 1.71.

4-((2,5-Diethynylphenyl)ethynyl)-N,N-dihexadecylaniline (M1)

To a 100 mL flask, (**2**) (1.00 g, 1.20 mmol), K_2CO_3 (0.50 g, 3.60 mmol), and MeOH (15 mL) were added, and the mixture was stirred at 20 ºC for 3 h. The mixture was diluted with DCM and the organic phase was washed three times with water. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and column chromatography (SiO_2, V_{hexane}/V_{DCM} = 10:1) yielded the desired (**M1**) (red solid, 0.70 g, 85%). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.86 (m, 6H), 1.26 (m, 52H), 1.55 (m, 4H), 3.13 (s, 1H), 3.25 (m, 4H), 3.39 (s, 1H), 6.54 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 10.0 Hz, 1H), 7.36 (d, J = 10.5 Hz, 2H), 7.42 (d, J = 5.5 Hz, 1H), 7.59 (s, 1H) ppm; FT-IR (KBr): ν = 3340, 2918, 2853, 2166, 1604, 1515, 1472, 1402, 1369, 1198, 1122, 1078, 1029, 865, 715 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{50}H_{75}N$: 689.62 g•mol^{-1},

found: 690.8 g•mol^{-1} [MH]$^+$; elemental analysis calcd (%) for C$_{50}$H$_{75}$N (689.62): C 87.16, H 10.80, N 2.04. found: C 87.15, H 10.82, N 2.03.
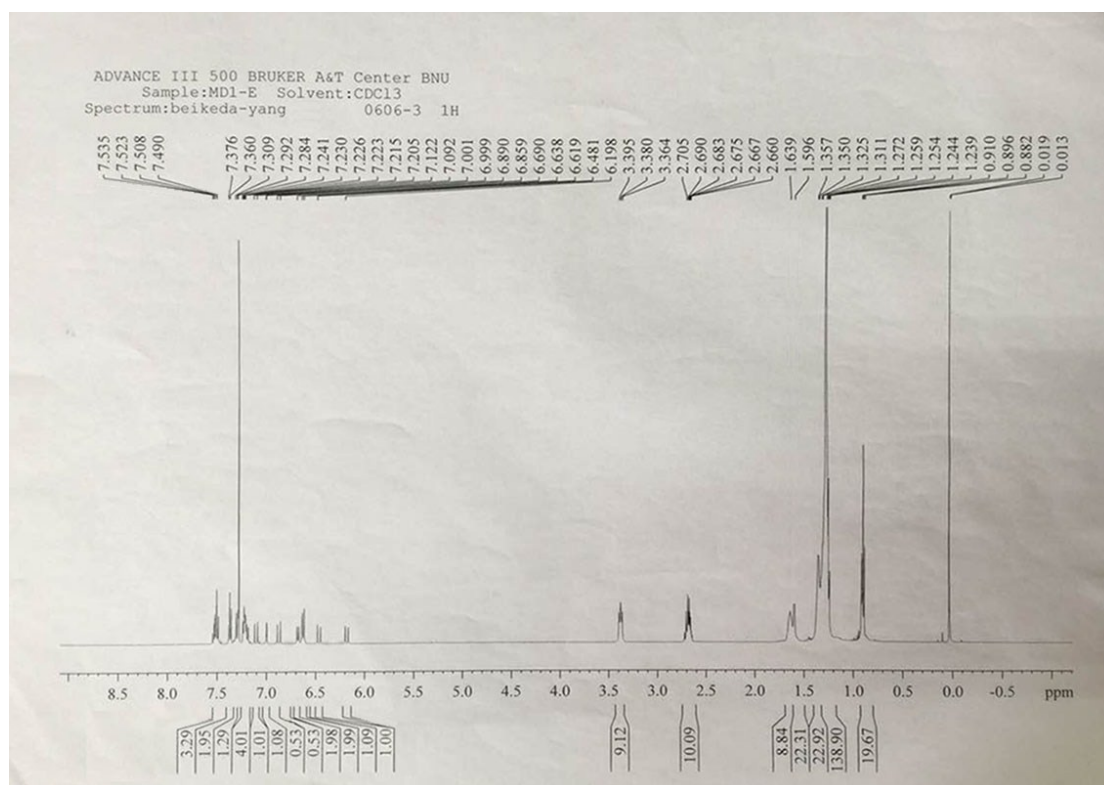
Model compound MD1

In a 50 mL two-necked flask equipped with a reflux condenser were placed Rh(PPh$_3$)$_3$Cl (0.015 mmol, 0.014 g), 1,2-dichloroethane (DCE) (5 mL), and monomer **(M1)** (0.25 mmol, 0.17 g) under argon (Ar) atmosphere. 4-Ethylthiophenol (0.55 mmol, 0.076 g) was added to the reaction solution at rt, and the reaction was stirred for 20 h with heating at 60 ºC. After the reaction was completed, the resulting mixture was concentrated, rediluted with dichloromethane (DCM), and filtered through a plug of silica gel. The solvent was removed in *vacuo* and the crude product was purified by column chromatography (SiO$_2$,V$_{hexane}$/V$_{DCM}$=8:1) to give **(MD1)** (red solid, 0.23 g, 95%). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ=0.88 (m, 12H), 1.26 (m, 52H), 1.60 (m, 4H), 2.67 (m, 4H), 3.29 (m, 4H), 6.55 - 6.57 (m, 3H), 6.90 (d, 15.5 Hz, 1H), 7.05 (s, 1H), 7.11 (d, 16.0 Hz, 1H), 7.16 (m, 1H), 7.19 (d, 8.5 Hz, 2H), 7.22 (d, 8.5 Hz, 2H), 7.29 (d, 9.0 Hz, 2H), 7.38 (d, 8.0 Hz, 2H), 7.41 (d, 6.5 Hz, 2H), 7.43 (d, 8.0 Hz, 2H) ppm; FT-IR (KBr): ν=2928, 2852, 2198, 1729, 1606, 1519, 1493, 1464, 1402, 1190, 1091, 1016, 938, 812 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{66}$H$_{95}$NS$_2$: 965.69 g·mol^{-1}, found: 965.8 g·mol^{-1} [M]; elemental analysis calcd (%) for C$_{66}$H$_{95}$NS$_2$: C 82.01, H 9.91, N 1.45. found: C 82.01, H 9.93, N 1.44.
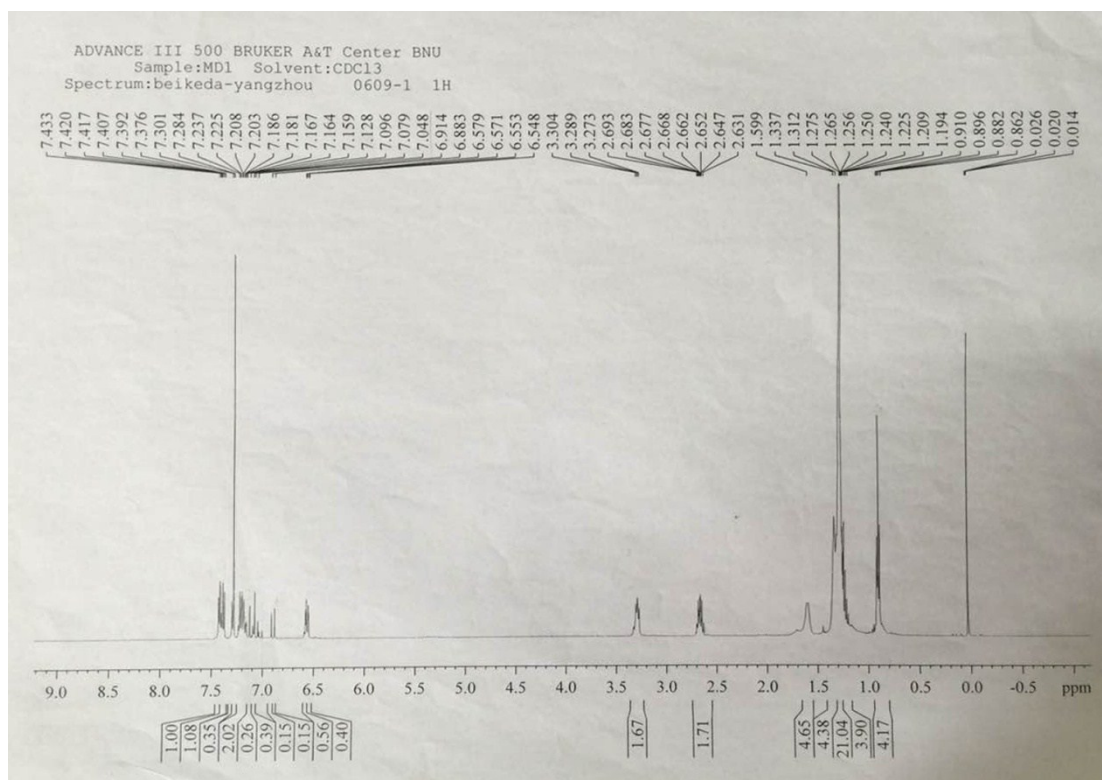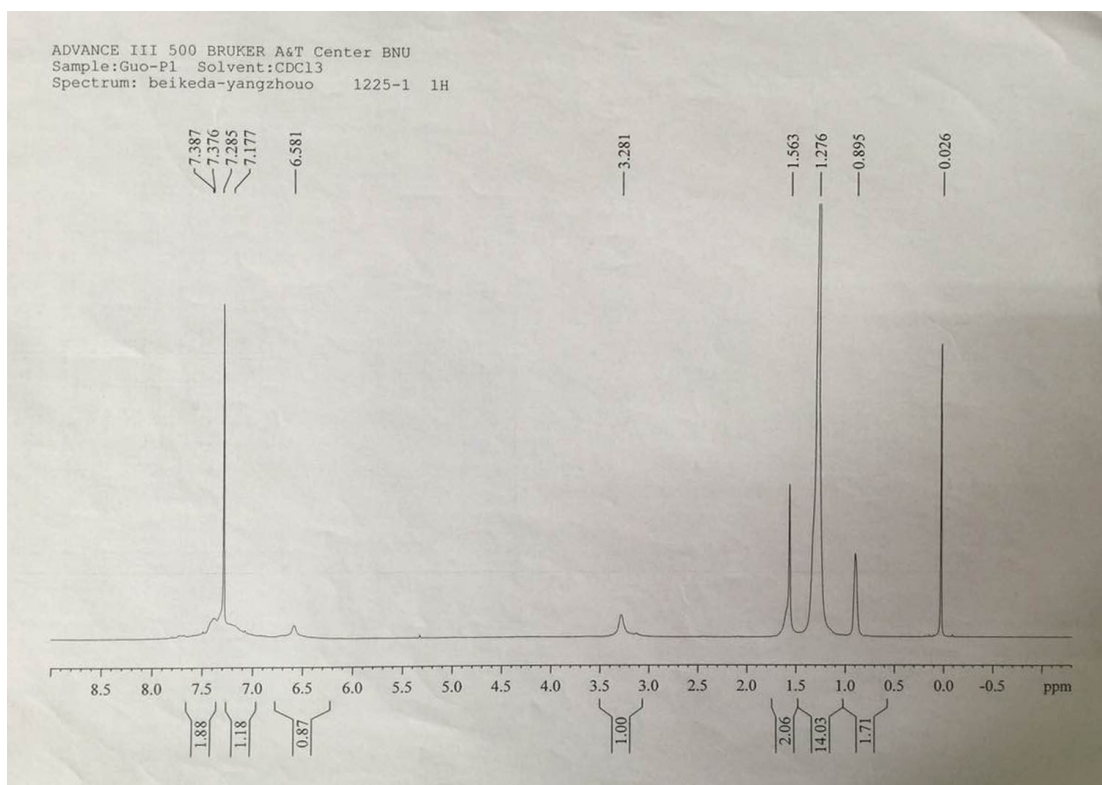
Model compound MD2

TCNE (0.053 mmol, 6.8 mg) was added to a solution of **(MD1)** (0.053 mmol, 50.0 mg) in DCM (4 mL), and the mixture was stirred for two hour at rt. Evaporation of the solvent and column chromatography (SiO$_2$, V$_{hexane}$/V$_{DCM}$=3:1) afforded the desired products (black solid, 52.0 mg, 92%). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ=0.88 (m, 12H), 1.26 (m, 52H), 1.64 (m, 4H), 2.69 (m, 4H), 3.38 (m, 4H), 6.18 (d, 15.5 Hz, 1H), 6.46 (d, 15.5 Hz, 1H), 6.63 (d, 9.5 Hz, 2H), 6.87 (d, 15.5 Hz, 1H), 7.00 (s, 1H), 7.11 (d, 15.0 Hz, 1H), 7.19 (d, 15.5 Hz, 1H), 7.22 (d, 9.0 Hz, 2H), 7.23 (d, 15.5 Hz, 1H), 7.30 (d, 8.5 Hz, 2H), 7.37 (d, 8.0 Hz, 2H), 7.50 (d, 9.0 Hz, 2H), 7.53 (d, 6.0 Hz, 2H) ppm; FT-IR (KBr): ν=2924, 2853, 2215, 1725, 1602, 1492, 1415, 1339, 1290, 1206, 1183, 1016, 936, 823 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{72}$H$_{95}$N$_5$S$_2$: 1093.70 g·mol^{-1}, found: 1094.5 g·mol^{-1} [MH]$^+$; elemental analysis calcd (%) for C$_{72}$H$_{95}$N$_5$S$_2$: C 79.00, H 8.75, N 6.40. found: C 78.98, H 8.76, N 6.39.

ADVANCE III 500 BRUKER A&T Center BNU
Sample:MD1-E   Solvent:CDCl3
Spectrum:beikeda-yang   0606-3   1H

Polymer P1

To an ampoule tube, monomer **(M1)** (0.25 mmol, 172.2 mg,), 4,4'-thiobisbenzenethiol (0.25 mmol, 62.5 mg), Rh(PPh$_3$)$_3$Cl (0.015 mmol, 13.9 mg) and DCE (3 mL) were added. The tube was attached to a vacuum line, sealed off, and then heated to 60 ºC for 24 h. After being cooled to rt, the solution was diluted with DCE (2 mL) and then poured into a large excess amount of methanol (MeOH). The precipitate was collected by filtration, washed with MeOH and dried in *vacuo*, yielding a yellow solid (158.0 mg, 67%). ^{1}H-NMR(CDCl$_3$, 500 MHz): δ=0.88 (m, 6H), 1.30 (br, 52H), 1.60 (br, 4H), 3.27 (br, 4H), 6.58 (br, 2H), 6.76-7.25 (br, 8H), 7.32-7.74 (br, 9H) ppm; FT-IR (KBr): ν=3306, 2923, 2852, 2199, 1605, 1519, 1473, 1393, 1369, 1188, 1096, 1011, 940, 812 cm^{-1}.

ADVANCE III 500 BRUKER A&T Center BNU
Sample:Guo-P1 Solvent:CDCl3
Spectrum: beikeda-yangzhouo   1225-1 1H

Polymer P2

To a solution of **(P1)** (0.053 mmol per repeat unit, 50.0 mg) in DCM (4 mL), a TCNE solution in DCE (6.8 mg, 1 mL) was added under Ar. The mixture was stirred at 20 ºC for 2 h. The solution was evaporated to afford **(P2)** (black solid, 49.4 mg, 87%). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ=0.89 (br, 6H), 1.30 (br, 52H), 1.65 (br, 4H), 3.37 (br, 4H), 6.62 (m, 2H), 6.80-7.25 (br, 6H), 7.31-7.67 (br, 10H), 7.74 (m, 1H) ppm; FT-IR (KBr): ν=3361, 2921, 2850, 2214, 1602, 1474, 1414, 1339, 1182, 1096, 1010, 937, 812 cm^{-1}.
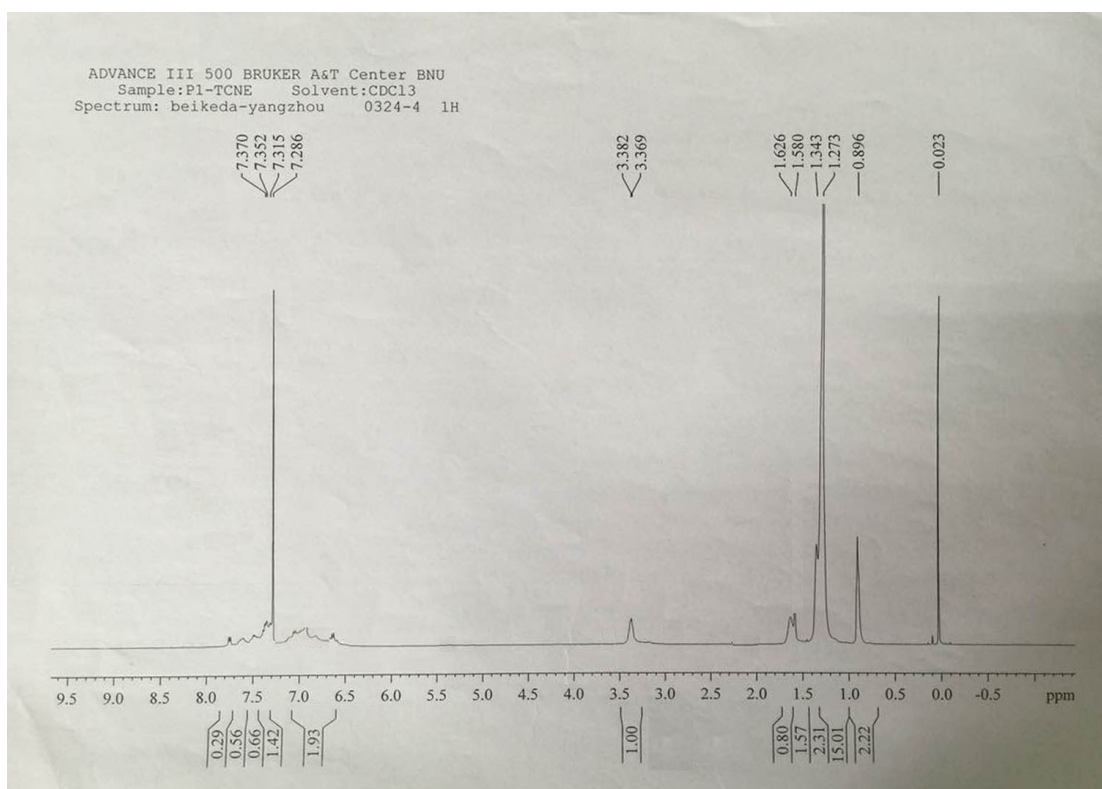
Electrochemical Test

The redox properties of all the novel compounds were investigated by cyclic voltammetry (CV) in dichloromethane (1×10^{-3} M, 0.1 M $n\mathrm{Bu_4NPF_6}$, all potentials vs. the ferricinium/ferrocene couple ($\mathrm{Fc^+/Fc}$)). The energy levels were calculated using the Ferrocene (Fc) value of -4.8 eV with respect to the vacuum level, which was defined as zero. The measured oxidation potential of Fc (vs Ag/AgCl) was 0.20 V. Therefore, the HOMO energy (E_{HOMO}) levels of the products could be calculated by the equation $E_{HOMO} = -e[E_{onset}(\mathrm{ox}) - E_{1/2,Fc} + 4.8\ \mathrm{V}]$ and the LUMO energy (E_{LUMO}) levels could be estimated by the equation $E_{LUMO} = -e[E_{onset}(\mathrm{red}) - E_{1/2,Fc} + 4.8\ \mathrm{V}]$, where $E_{1/2,Fc}$ standards for the half-wave potential of $\mathrm{Fc/Fc^+}$.

NLO Calculation

In theory [1-3], the normalized transmittance for the open aperture can be written as:

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1 \tag{1}$$

where $q_0(z) = \dfrac{\alpha I(t) L_{eff}}{1 + Z^2/Z_0^2}$, α is the nonlinear absorption coefficient, $I_0(t)$ is the intensity of laser beam at focus (z =0), $L_{eff} = |1 - \exp(-\alpha_0 L)|/\alpha_0$ is the effective thickness with α_0 the linear absorption coefficient and L the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. Thus, the nonlinear absorption coefficients of the compounds can be determined by fitting the experimental data using Eq. (1).

The normalized transmission for the closed aperture Z-scan is given by the following:

$$T = 1 + \frac{4\Delta\Phi_0 x}{(x^2 + 9)(x^2 + 1)} \tag{2}$$

where x =z/z_0 and $\Delta\Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\Phi = 2\pi n_2 I_0 L_{eff}/\lambda$. Thus, the nonlinear refractive coefficients of the compounds can be determined by fitting the experimental data using Eq.(2).

The $\chi^{(3)}$ can be calculated by Eq.(3):

$$|\chi(3)| = \sqrt{\left|\frac{n_0^2 c}{120\pi^2}n_2\right|^2 + \left|\frac{c^2 n_0^2}{240\pi^2 \omega}\beta\right|^2} \tag{3}$$

where $\omega = 2\pi c/\lambda$, c is the speed of light, n_0 is the refractive e index of the medium.

References:

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