Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary Information

Manipulation of Quantum Interference by Charge Accumulation in Conjugated Structure

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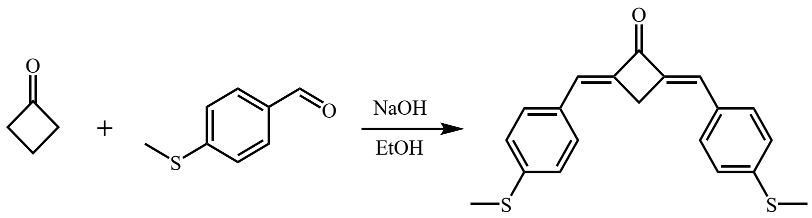
1. Synthesis and Characterization

Physical Measurement. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 M NMR spectrometer with $SiMe_4$ as the internal reference. All coupling constants are absolute values, and the J values are expressed in hertz (Hz). The description of the signals includes s = singlet, d = doublet, t = triblet and m = multiplet. Mass spectra were recorded on an Agilent Q−TOF 6520 system using electrospray ionization in Positive/Negative ion detection (ESI+/ESI−) mode.

General Procedures and Reagents. All the manipulations were carried out using Schlenk techniques and vacuum-line systems under a dry argon atmosphere unless otherwise specified. All reagents including dichloromethane (DCM) and petroleum ether (PE) were of commercial origin and were used as received. The Ethanol (EtOH) was distilled from benzophenone prior to use. Silica gel (100-200 mesh) was used for the column chromatography.

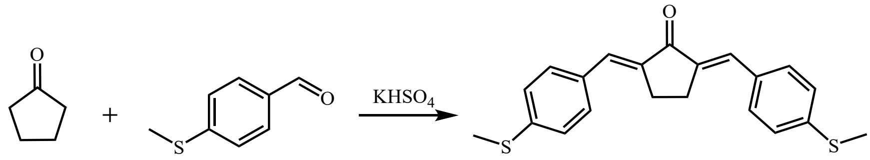
1.1 Experimental Procedures

2,4-bis[*E*-4-(methylthio)benzylidene]cyclobutan-1-one (*c*-PDO-1)[1]:



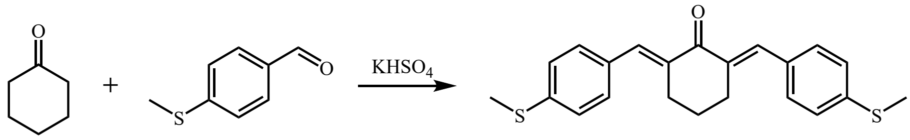
Under nitrogen atmosphere, a solution of cyclobutanone (0.70 g, 10.0 mmol) in EtOH (4.0 mL) was added dropwise with stirring at 5°C to a mixture of 4-(methylthio)benzaldehyde (3.04 g, 20.0 mmol) and a NaOH solution (0.25 M) in an EtOH – H_2O mixture (2 : 1 *v* / *v*) (7.0 mL) and stirred at 5°C for 20 h. Then after adding Et_2O (20 mL), the precipitate was filtered and recrystallized in dichloromethane/ethanol to produce 1.45 g (4.3 mmol) of yellow solid. Yield: 42.8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.52 Hz, 4H), 7.28 (d, J = 6.48 Hz, 4H), 7.20 (t, J = 2.6 Hz, 2H), 3.82 (t, J = 2.6 Hz, 2H), 2.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.27, 146.03, 142.63, 132.89, 130.26, 127.80, 126.47, 35.32, 16.05. HR-MS (ESI): calcd. for $C_{20}H_{19}OS_2$ $[M+H]^+$: 339.0872; found: 339.0871.

2,5-bis[*E*-4-(methylthio)benzylidene]cyclopentan-1-one (*c*-PDO-2)[2]:



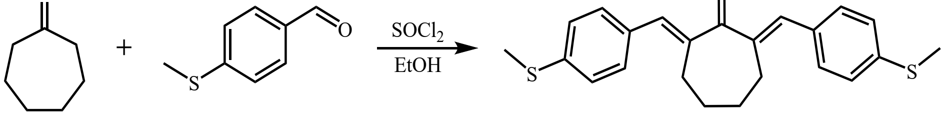
Under nitrogen atmosphere, cyclopentanone (0.42 g, 5.0 mmol), $KHSO_4$ (0.07 g, 0.5 mmol), 4-(methylthio)benzaldehyde (1.52 g, 10.0 mmol) were added successively, and stirred at 90°C overnight. After cooling to room temperature, the resulting solution was diluted with water (60 mL) and extracted by dichloromethane (3 × 60 mL). After being dried with Na_2SO_4, the organic phase was removed under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether: dichloromethane = 1:1 as eluent to afford 0.58 g (1.6 mmol) yellow solid. Yield: 31.2%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.53 (d, J = 8.64 Hz, 4H), 7.28 (d, J = 8.52 Hz, 4H), 3.10 (s, 4H), 2.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.23, 141.16, 137.62, 133.85, 132.48, 131.20, 125.96, 26.66, 15.22. HR-MS (ESI): calcd. for $C_{21}H_{21}OS_2$ $[M+H]^+$: 353.1028; found: 353.1027.

2,6-bis[*E*-4-(methylthio)benzylidene]cyclohexan-1-one (*c*-PDO-3)[2]:



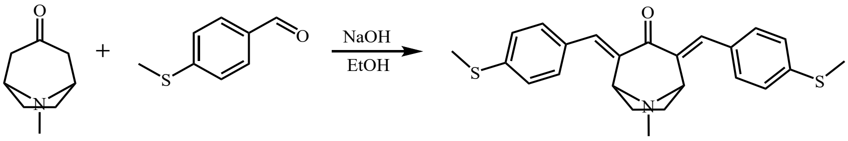
Under nitrogen atmosphere, cyclohexanone (0.49 g, 5.0 mmol), $KHSO_4$ (0.07 g, 0.5 mmol), 4-(methylthio)benzaldehyde (1.67 g, 11.0 mmol) were added successively, and stirred at 90°C overnight. After cooling to room temperature, the resulting solution was diluted with water (60 mL) and extracted by dichloromethane (3 × 60 mL). After being dried with Na_2SO_4, the organic phase was removed under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether: dichloromethane = 1:1 as eluent to afford 0.95 g (2.6 mmol) yellow solid. Yield: 51.8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.40 (d, J = 8.4 Hz, 4H), 7.26 (d, J = 8.52 Hz, 4H), 2.92 (t, J = 5.24 Hz, 4H), 2.51 (s, 6H), 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.10, 166.28, 140.56, 136.44, 135.55, 132.53, 130.93, 126.09, 29.08, 23.67, 13.97. HR-MS (ESI): calcd. for $C_{22}H_{23}OS_2$ $[M+H]^+$: 367.1185 ; found: 367.1182.

2,7-bis[*E*-4-(methylthio)benzylidene]cycloheptan-1-one (*c*-PDO-4)[3]:



Under nitrogen atmosphere, Thionyl chloride (0.23 g, 1.96 mmol) and cycloheptanone (0.55 g, 4.9 mmol) were added to an ethanol solution (0.71 mL) containing 4-(methylthio)benzaldehyde (1.48 g, 9.8 mmol) at 0°C for 3-5 min, then slowly heat up to room temperature for 2 h. And being neutralized with saturated potassium bicarbonate solution, the resulting solution was diluted with water (60 mL) and extracted by dichloromethane (3 × 60 mL). After being dried with Na_2SO_4, the organic phase was removed under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether: ethyl acetate = 5:1 as eluent to afford 0.84 g (2.2 mmol) yellow solid. Yield: 45.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 5.64 Hz, 4H), 7.24 (s, 2H), 7.16 (d, J = 5.44 Hz, 4H), 2.60 (m, 4H), 2.41 (s, 6H), 1.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.73, 141.09, 139.29, 135.16, 132.48, 130.06, 125.98, 28.63, 28.19, 15.38. HR-MS (ESI): calcd. for $C_{23}H_{25}OS_2$ $[M+H]^+$: 381.1341; found: 381.1338.

8-methyl-2,4-bis[*E*-4-(methylthio)benzylidene]-8-azabicyclo[3.2.1]octan-3-one (*c*-PDO-4-N)^4:

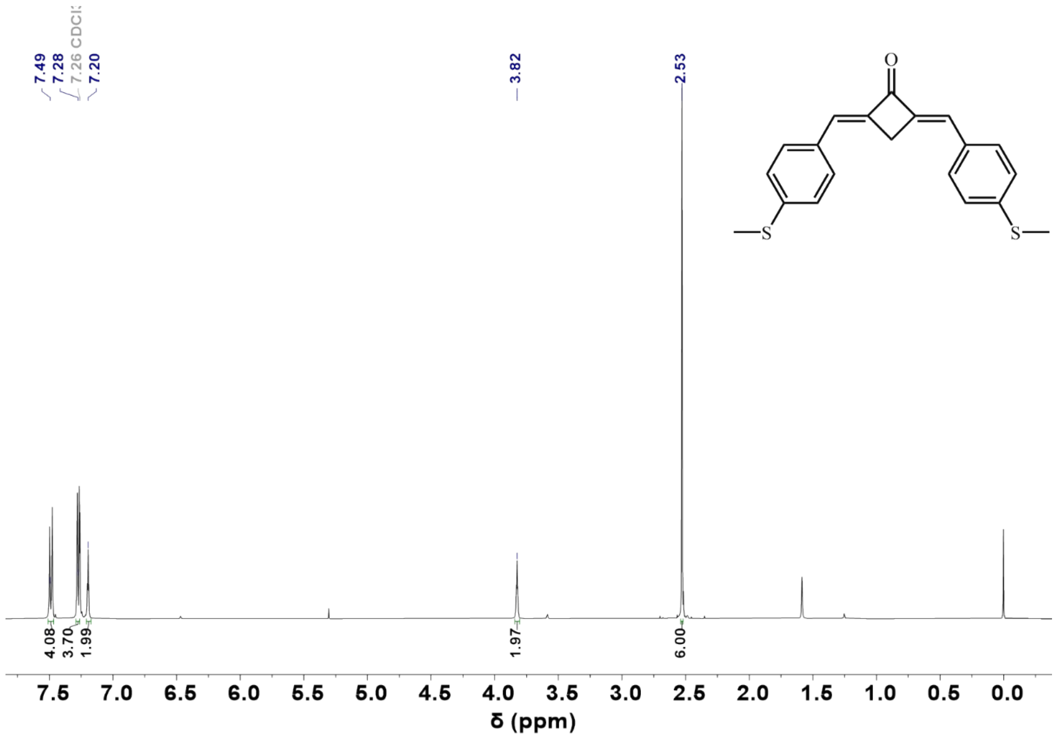


Under nitrogen atmosphere, The NaOH solution (2 mL, 10%) is added to the 4-(methylthio)benzaldehyde (0.45 g, 2.9 mmol) dissolved in ethanol (8.7 mL), tropinone (0.21 g, 1.5 mmol) dissolved in ethanol (2.9 mL) is added drop by drop to the mixture, which then stirred at room temperature overnight. Yellow precipitates were filtered and washed with saturated sodium chloride. The residue was dissolved in a small amount of dichloromethane, which was then dried with Na_2SO_4. The organic phase was removed under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether: ethyl acetate = 5:1 as eluent to afford 0.25 g (0.61 mmol) yellow solid. Yield: 40.9%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.31 (d, J = 8.56 Hz, 4H), 7.28 (d, J = 8.2 Hz, 4H), 4.39 (m, 2H), 2.61 (m, 2H), 2.51 (s, 6H), 2.30 (s, 3H), 2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.86, 141.20, 137.69, 136.14, 133.19, 130.31, 125.18, 62.52, 39.05, 30.27, 14.61. HR-MS (ESI): calcd. for $C_{24}H_{26}OS_2N$ $[M+H]^+$: 408.1450; found: 408.1445.

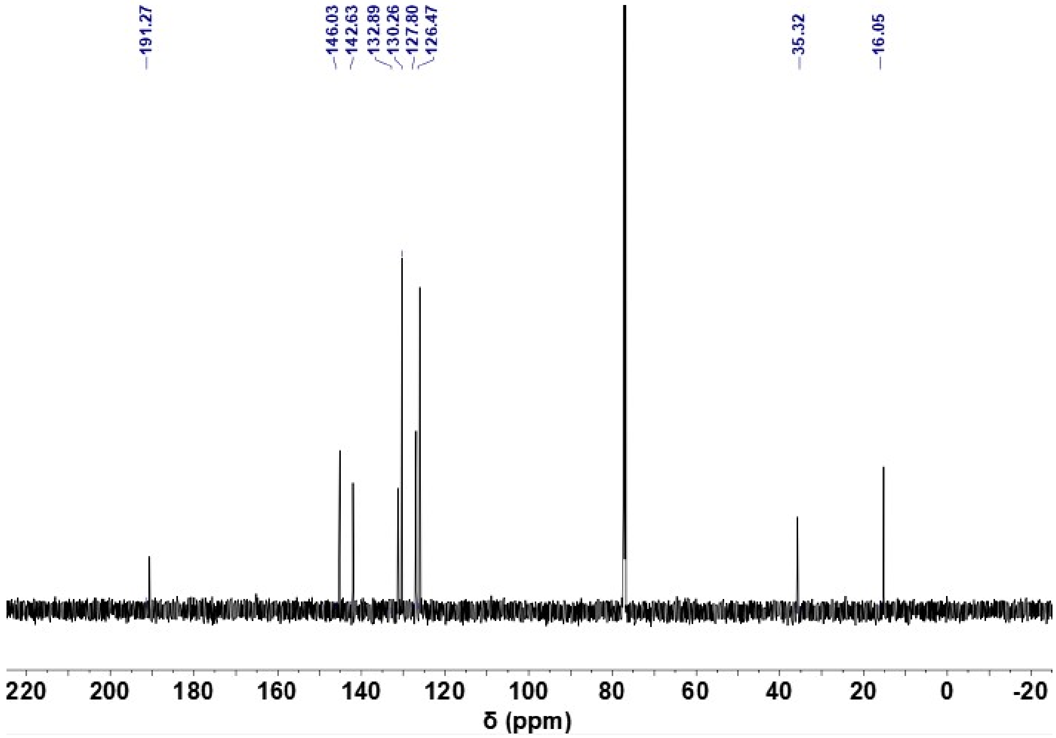
1.2 Characterization

c-PDO-1

^{1}H NMR

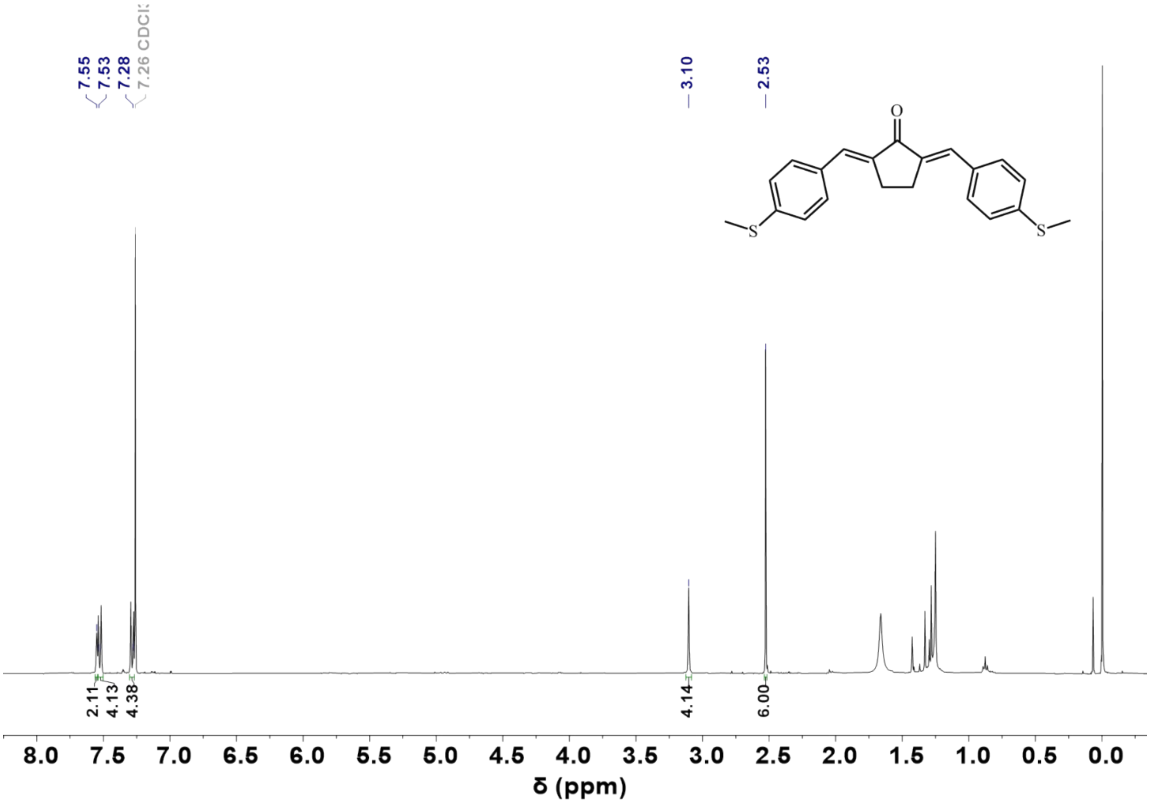


^{13}C NMR

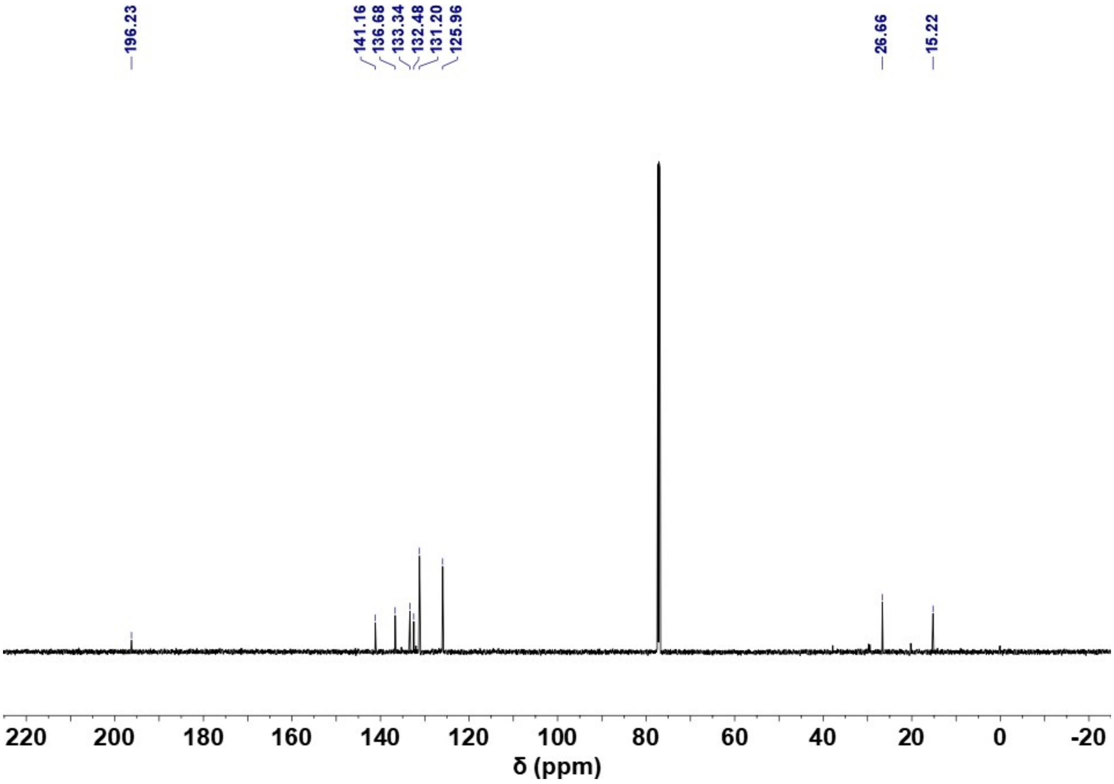


***c*-PDO-2**

^{1}H NMR

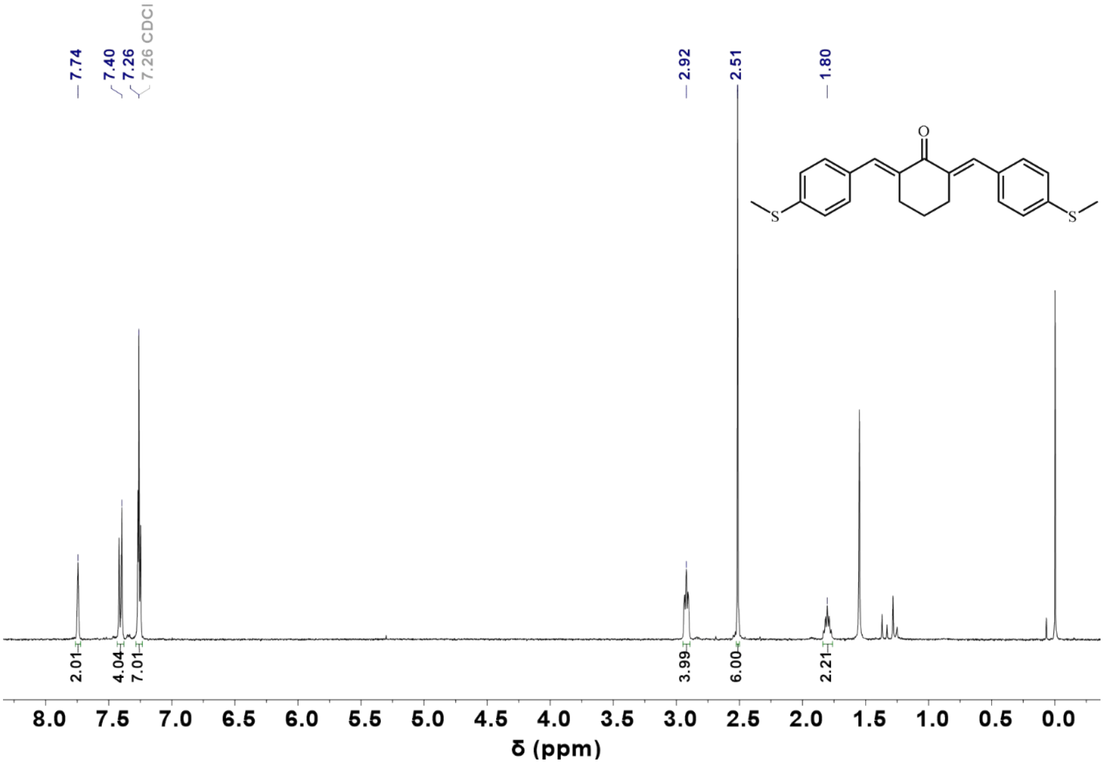


^{13}C NMR

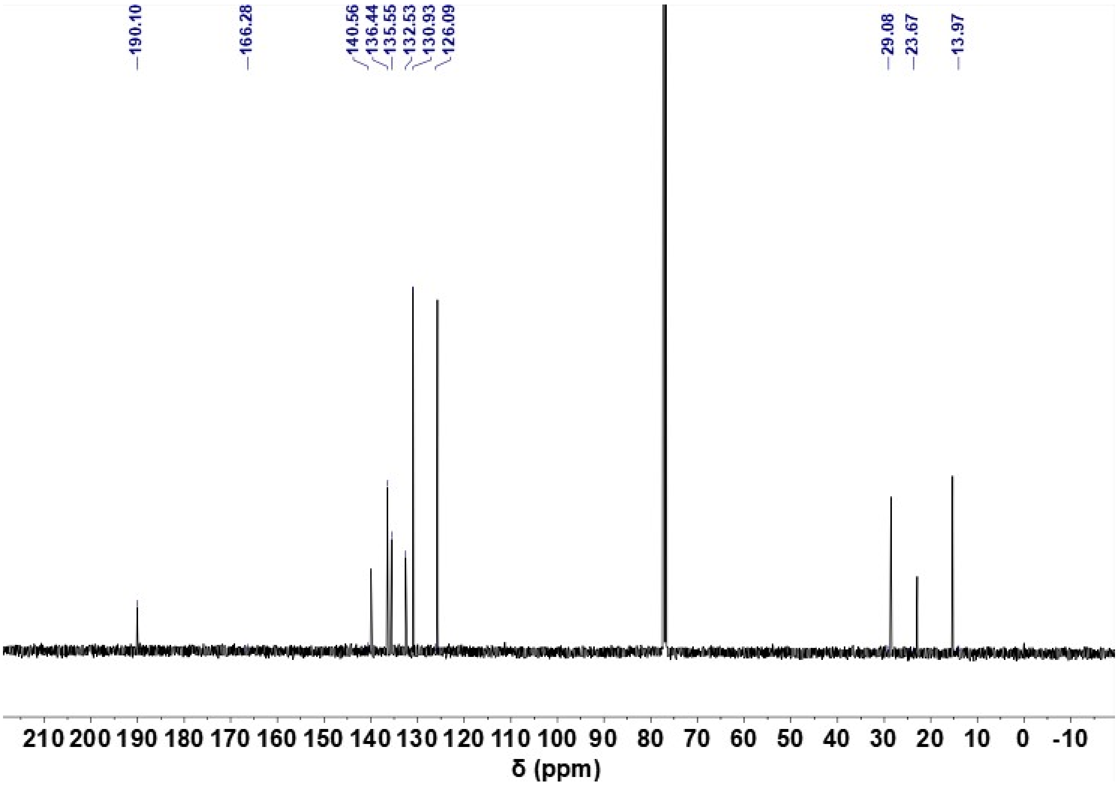


***c*-PDO-3**

^{1}H NMR

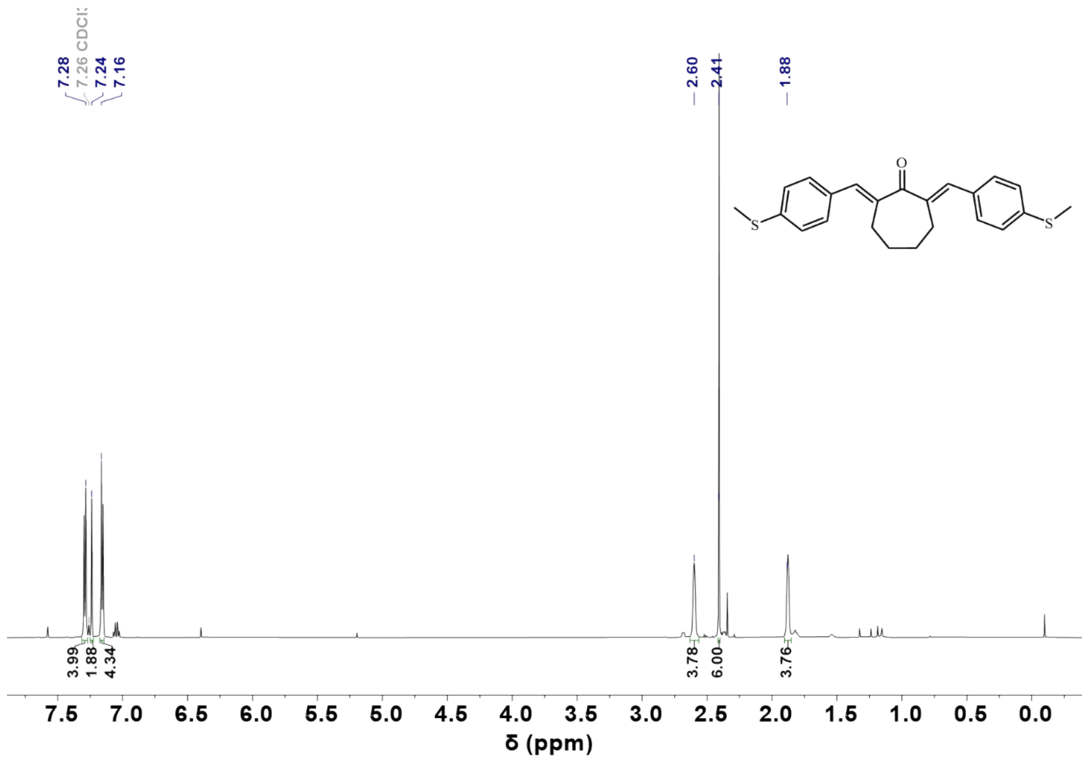


^{13}C NMR

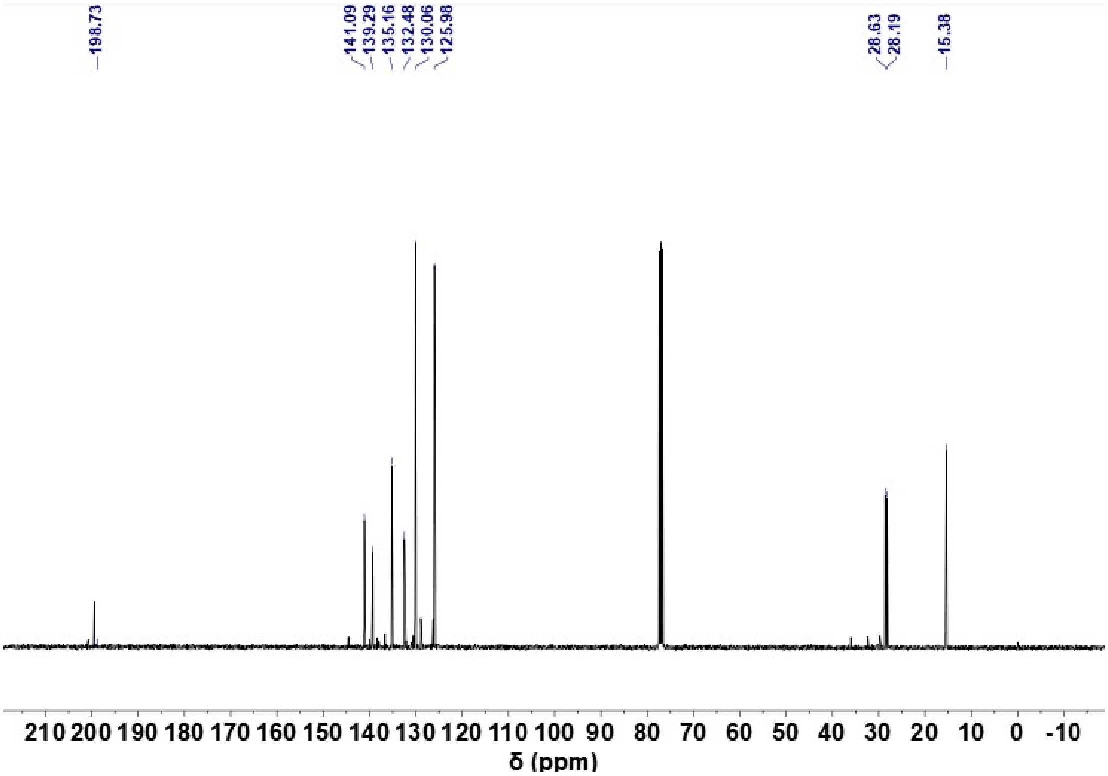


c-**PDO-4**

^{1}H NMR

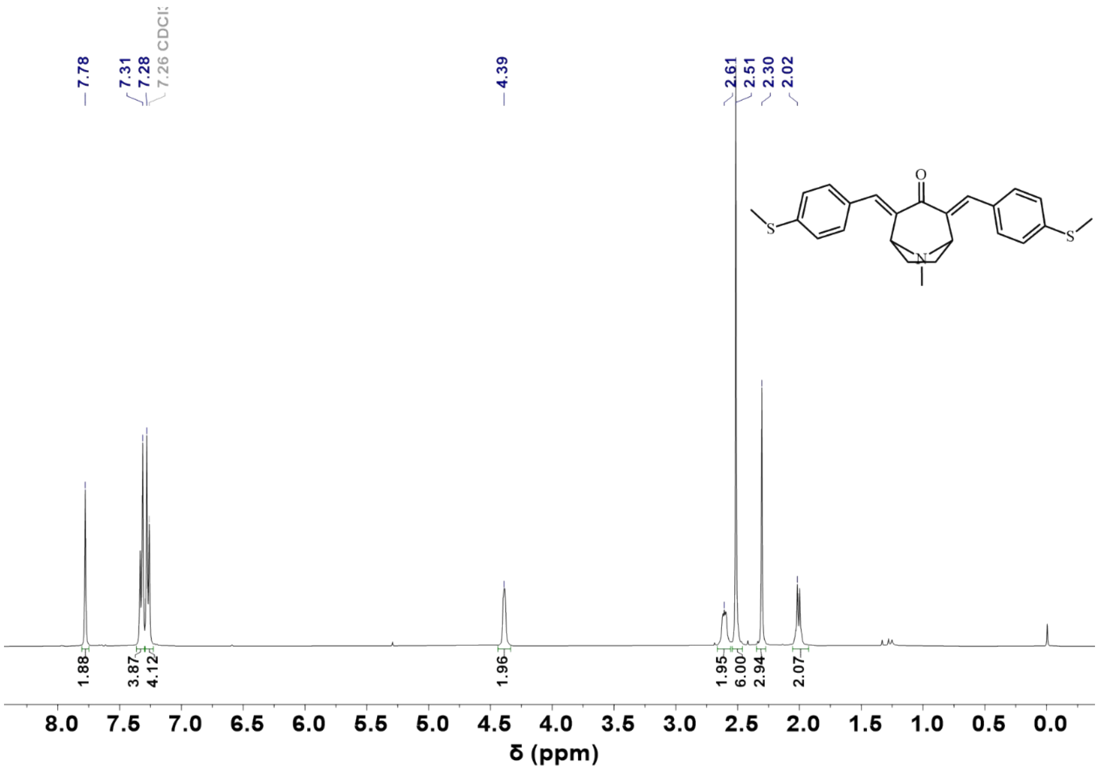


^{13}C NMR

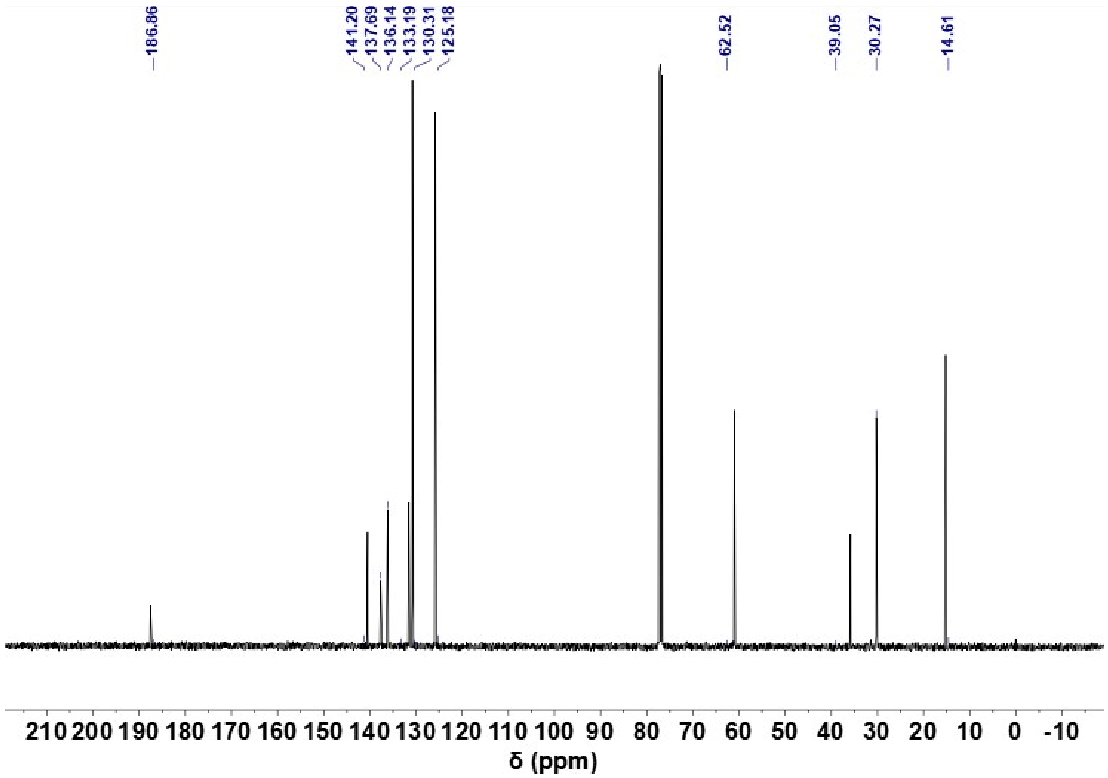


***c*-PDO-4-N**

^{1}H NMR

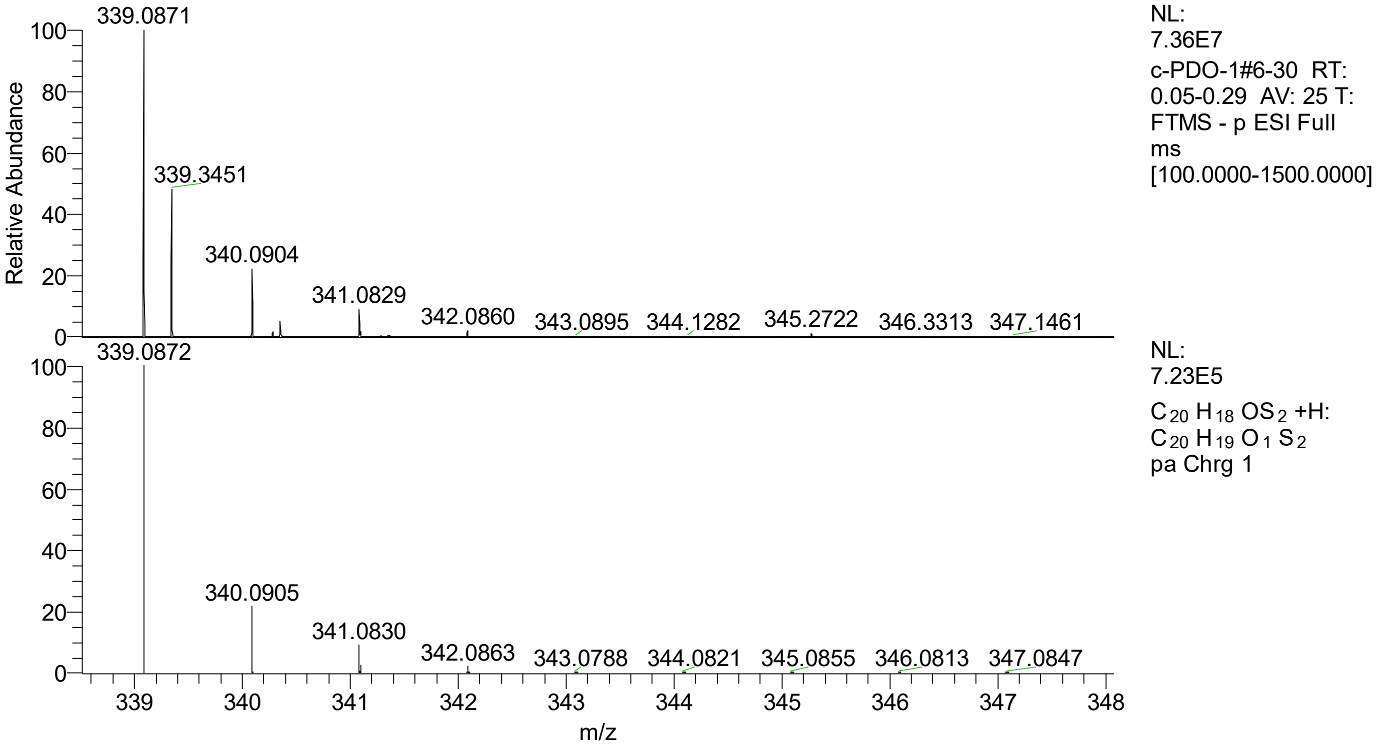


^{13}C NMR

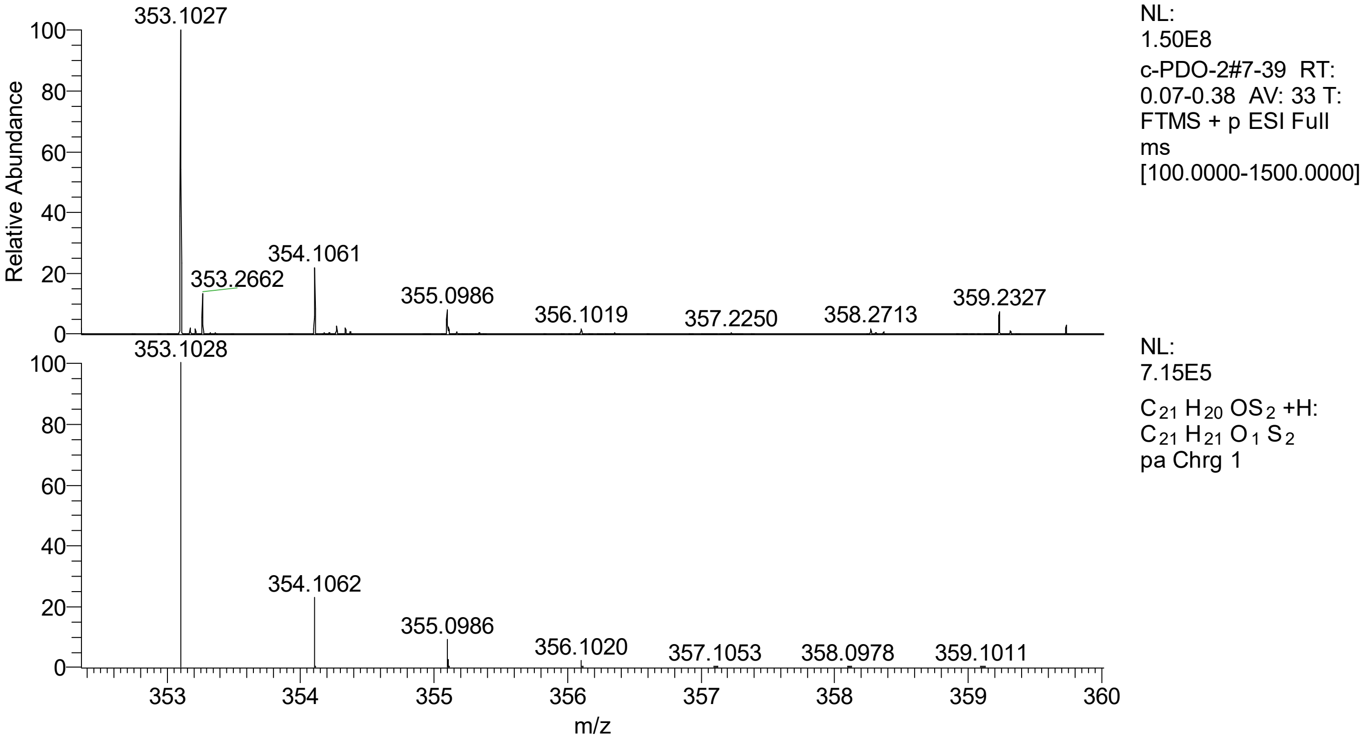


HR-MS

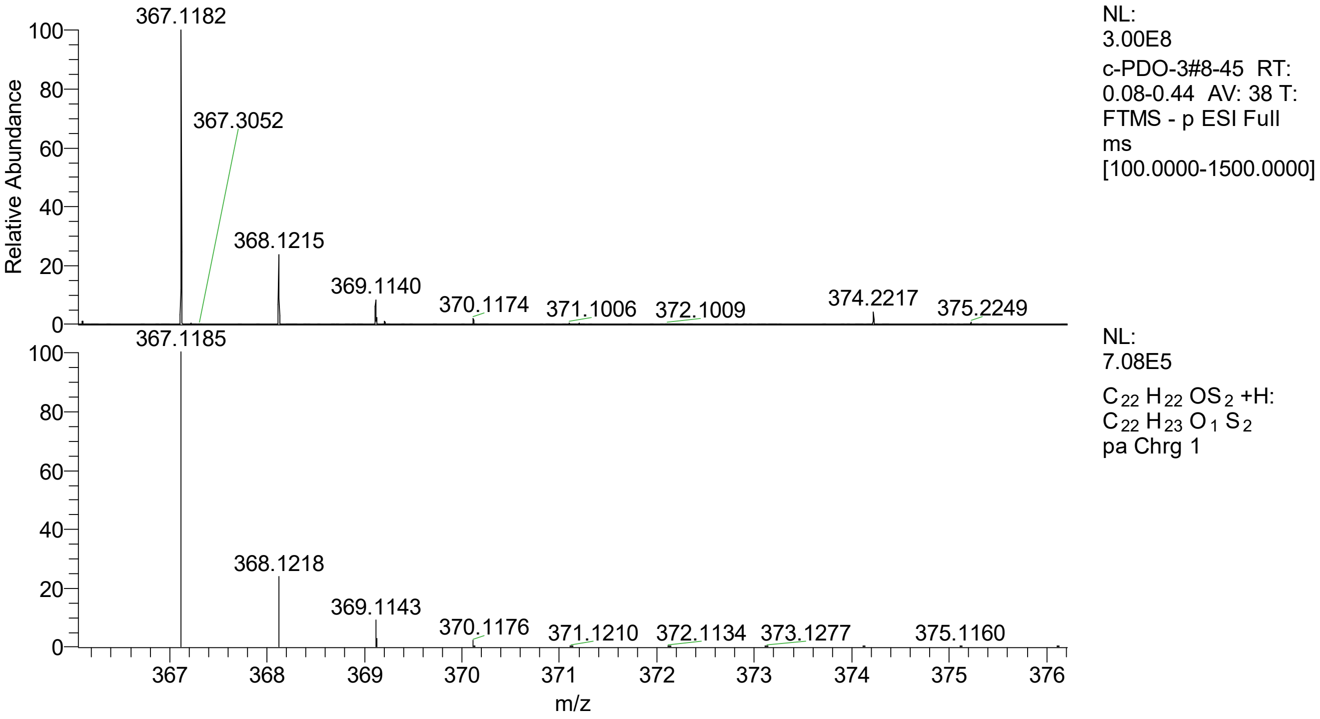
c-PDO-1



c-PDO-2



c-PDO-3


367.1182
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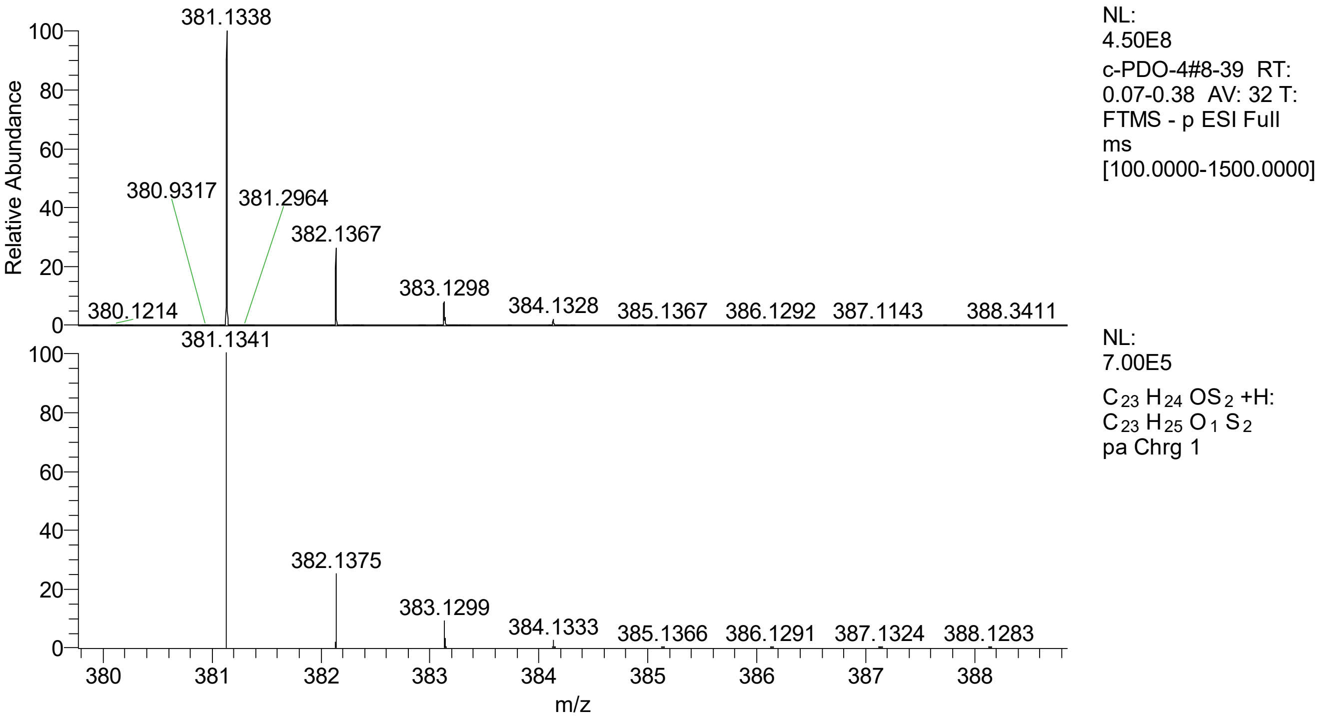
368.1215
369.1140
370.1174
371.1006
372.1009
374.2217
375.2249
367.1185
368.1218
369.1143
370.1176
371.1210
372.1134
373.1277
375.1160
Relative Abundance
100
80
60
40
20
0
367
368
369
370
371
372
373
374
375
376
m/z
NL:
3.00E8
c-PDO-3#8-45 RT: 0.08-0.44 AV: 38 T: FTMS - p ESI Full ms [100.0000-1500.0000]
NL:
7.08E5
$C_{22}H_{22}OS_2$ +H:
$C_{22}H_{23}O_1S_2$
pa Chrg 1

c-PDO-4


381.1338
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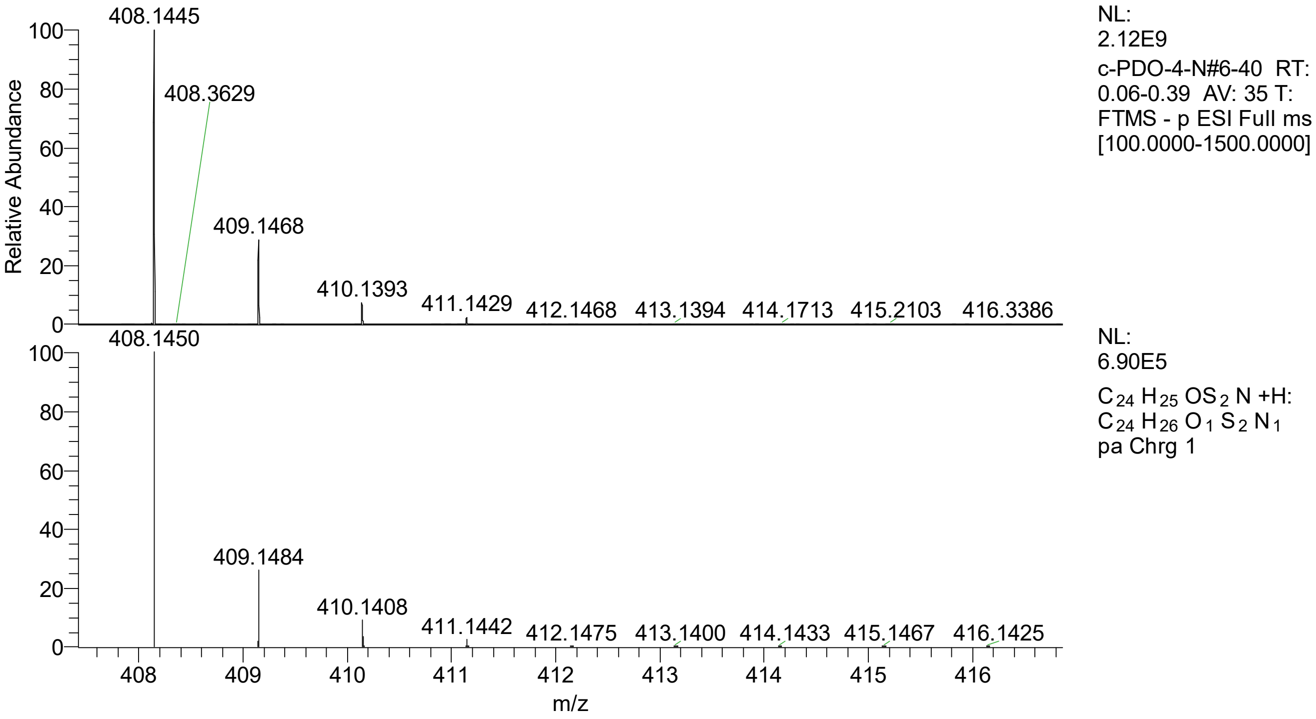
384.1328
385.1367
386.1292
387.1143
388.3411
381.1341
382.1375
383.1299
384.1333
385.1366
386.1291
387.1324
388.1283
Relative Abundance
100
80
60
40
20
0
380
381
382
383
384
385
386
387
388
m/z
NL:
4.50E8
c-PDO-4#8-39 RT: 0.07-0.38 AV: 32 T: FTMS - p ESI Full ms [100.0000-1500.0000]
NL:
7.00E5
$C_{23}H_{24}OS_2$ +H:
$C_{23}H_{25}O_1S_2$
pa Chrg 1

c-PDO-4-N



2. Transport Measurements

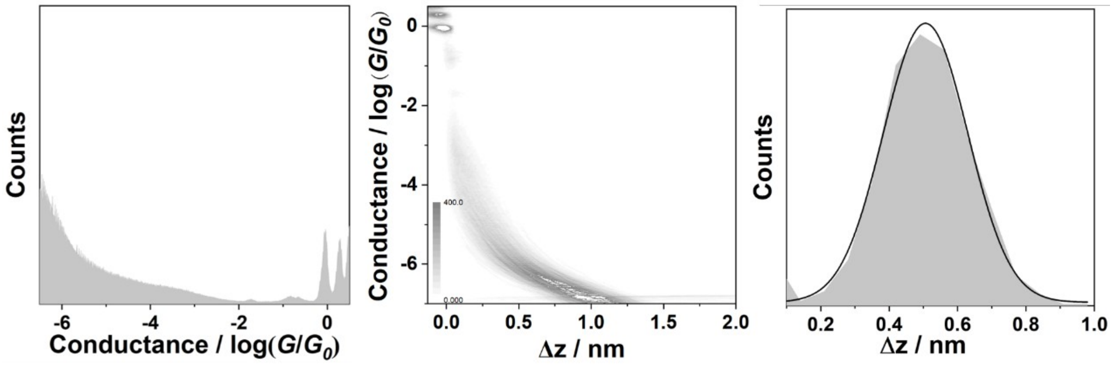


Fig. S1 One-dimension conductance histogram, two-dimension conductance histogram and the relative displacement distribution determined from $10^{0.3}$ G_0 to $10^{-6.0}$ G_0 for the calibration of the stretching rate of the electrodes pair.

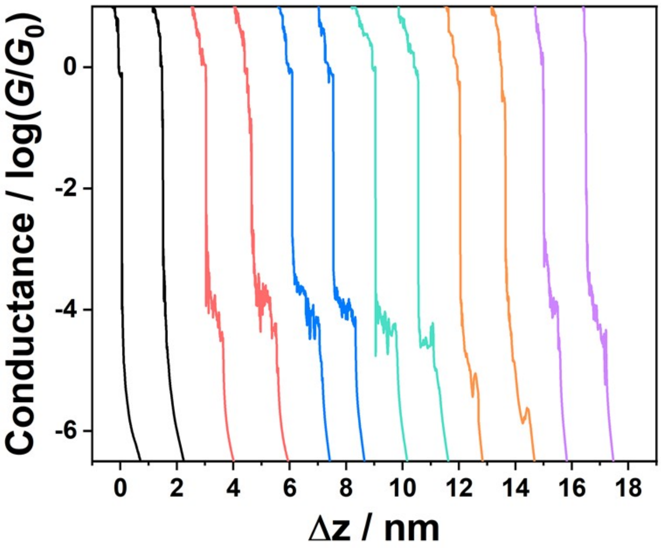


Fig. S2 Typical individual traces of pure solvent (black line), ***c*-PDO-1** (pink line), **c-PDO-2** (blue line), ***c*-PDO-3** (green line), ***c*-PDO-4** (orange line), ***c*-PDO-4-N** (purple line).

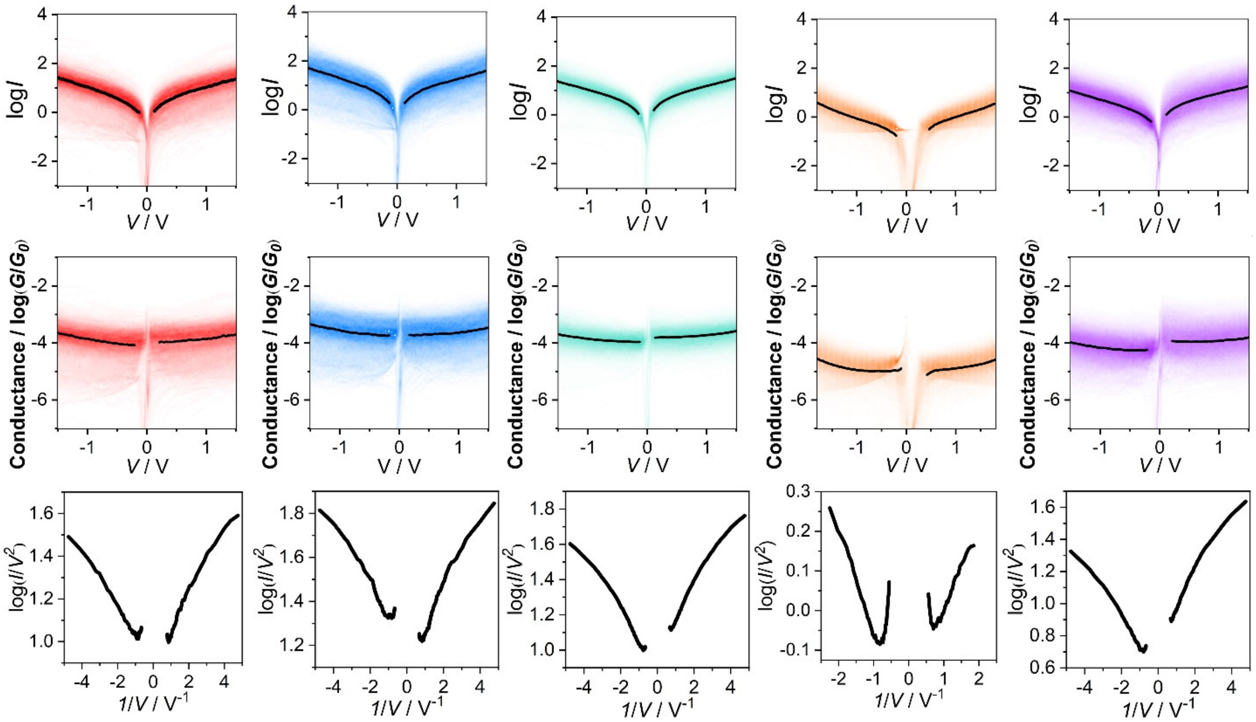


Fig. S3 a) Semilog plot of the *I*-*V* scanning, b) semilog plot of the *G*-*V* scanning, c) TVS plot for ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4** and ***c*-PDO-4-N**.

The method of obtaining the energy offset from TVS is to use the asymmetric coupling formula of the following single-level model.

$$E = \frac{2\left|V_t^+ - V_t^-\right|}{\sqrt{\left(V_t^+\right)^2 + \left(V_t^-\right)^2 + \frac{10\left|V_t^+ V_t^-\right|}{3}}} \quad (1)$$

The energy offset obtained from TVS corresponds to the difference between the Fermi energy (E_F) and the nearest frontier orbital level, while the UV-Vis absorption spectrum reflects the energy difference between the ground state and excited state (usually HOMO-LUMO gap in organic molecules). Since the E_F is usually located between HOMO and LUMO, the energy offset is equal or less than half of the HOMO-LUMO gap as it is only a part of the HOMO-LUMO gap. However, there's no functional relationship between these two energy values.

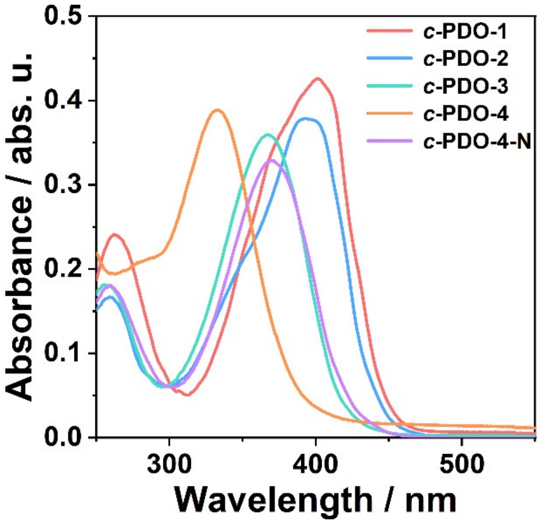


Fig. S4 Ultraviolet absorption spectra of ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4** and ***c*-PDO-4-N** in THF solution (10^{-5} M).

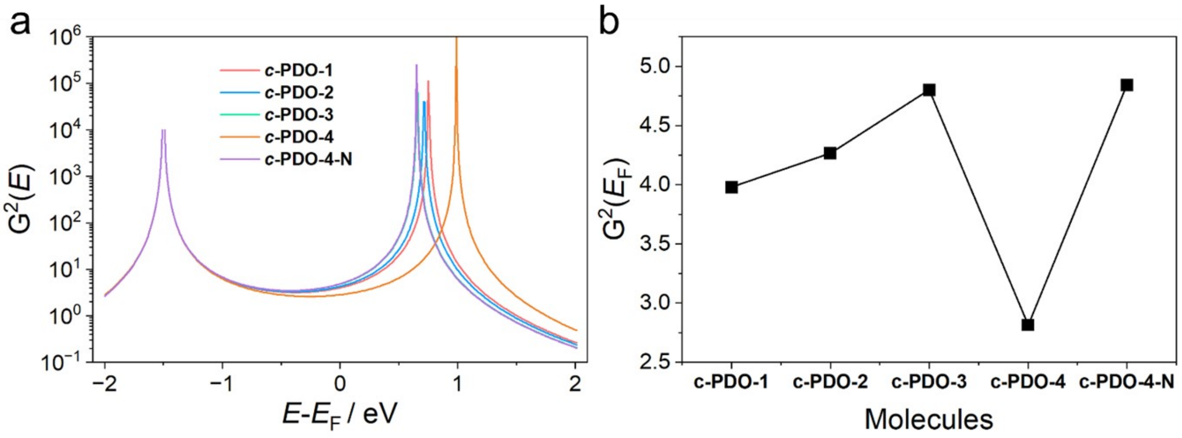


Fig. S5 a) Simulation of Green's function using two orbitals (HOMO:LUMO), where parameters are set as "HOMO": orbital coefficient = -1, E = -1.5 eV and "LUMO": orbital coefficient = -1, energy levels are set according to the energy offsets result in TVS; b) Simulated Green’s function at Fermi energy for each molecule.

3. Theoretical Calculations

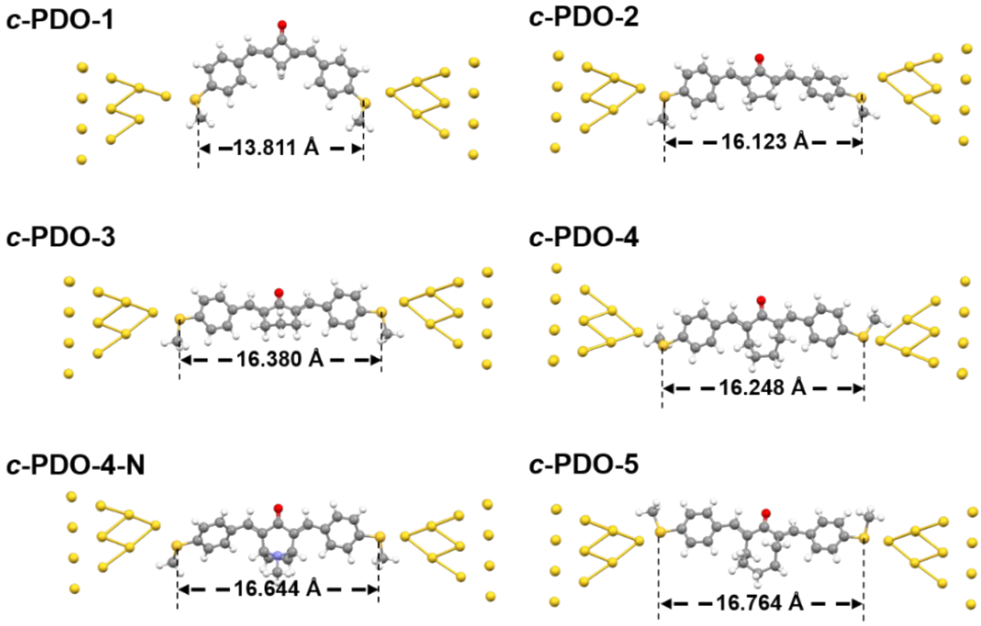


Fig. S6 The optimized molecular structure and the distance (Å) between anchoring groups of ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4**, ***c*-PDO-4-N** and ***c*-PDO-5**.

Table S1 The conductance, break-off distance (experimental and theoretical) and junction formation probability of ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4** and ***c*-PDO-4-N**.

Compound	Conductance / log (G/G_0)		Break-off distance / nm		Junction formation probability
	Exp	Theo	Exp	Theo	
***c*-PDO-1**	-4.19	-2.15	1.31	1.38	68.33%
***c*-PDO-2**	-3.90	-1.94	1.33	1.61	75.76%
***c*-PDO-3**	-4.25	-2.36	1.35	1.64	67.24%
***c*-PDO-4**	-5.46	-2.95	1.44	1.62	64.27%
***c*-PDO-4-N**	-4.52	-2.06	1.24	1.66	75.58%

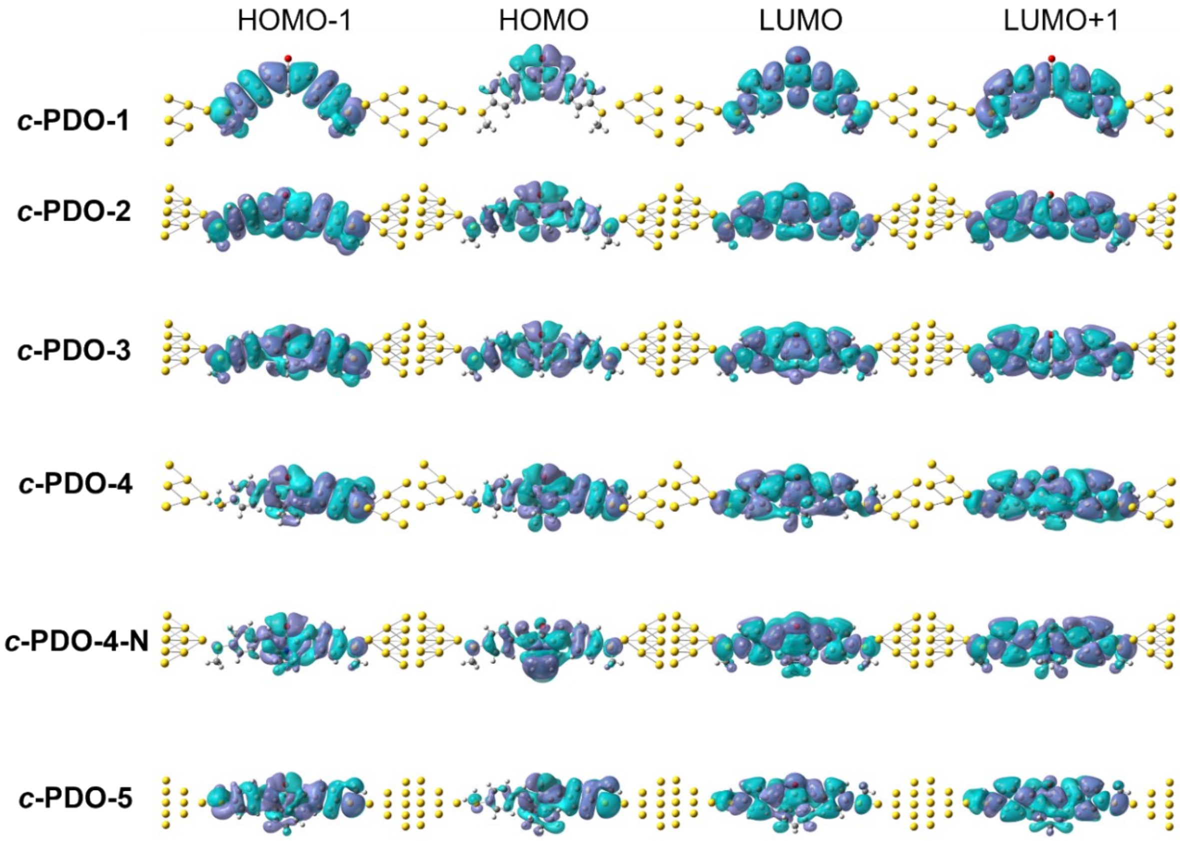


Fig. S7 MOs for ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4**, ***c*-PDO-4-N**, and ***c*-PDO-5** with the isovalent = 0.005 to show the orbital on the anchor groups.

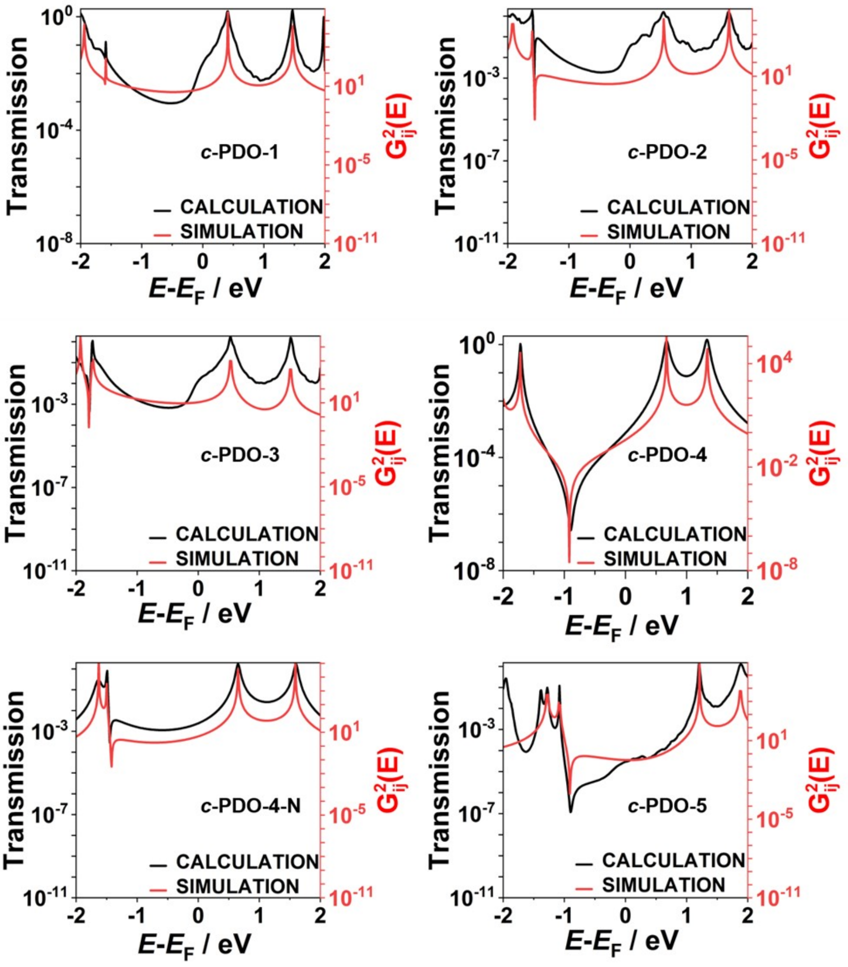


Fig. S8 Fitting of $T(E)$ using HOMO-1:HOMO:LUMO:LUMO+1.

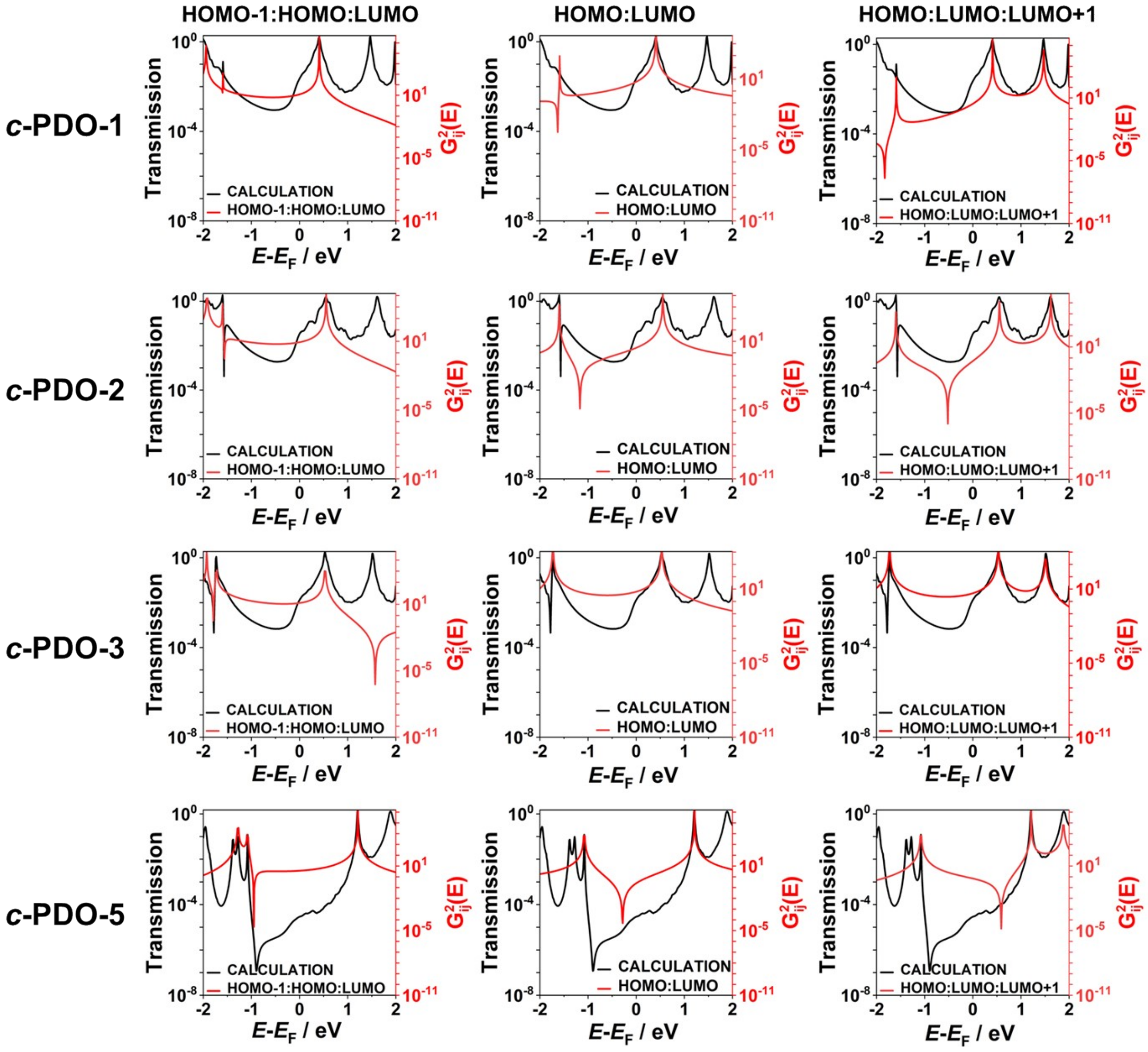


Fig. S9 Fitting of *T*(*E*) using HOMO-1:HOMO:LUMO, HOMO:LUMO and HOMO:LUMO:LUMO+1 (Fig. 3 consists of the fitting of ***c*-PDO-4** and ***c*-PDO-4-N**) .

Table S2. The energy level and the coefficients of the corresponding molecular orbital.

	$E_{\mathrm{LUMO+1}}$	E_{LUMO}	E_{HOMO}	$E_{\mathrm{HOMO-1}}$	$\alpha_{\mathrm{LUMO+1}}$	α_{LUMO}	α_{HOMO}	$\alpha_{\mathrm{HOMO-1}}$
***c*-PDO-1**	1.47	0.41	-1.59	-1.94	-1.2	1	-0.02	-2
***c*-PDO-2**	1.62	0.55	-1.60	-1.92	-1.50	1	0.25	-2.4
***c*-PDO-3**	1.51	0.53	-1.73	-1.93	-0.5	1	-1	-2.3
***c*-PDO-4**	1.34	0.67	-1.72	-2.05	-1.12	1	0.376	-0.44
***c*-PDO-4-N**	1.59	0.65	-1.50	-1.63	-2	2	0.45	-1.2
***c*-PDO-5**	1.88	1.21	-1.08	-1.28	-2.5	1.5	0.8	-1.8

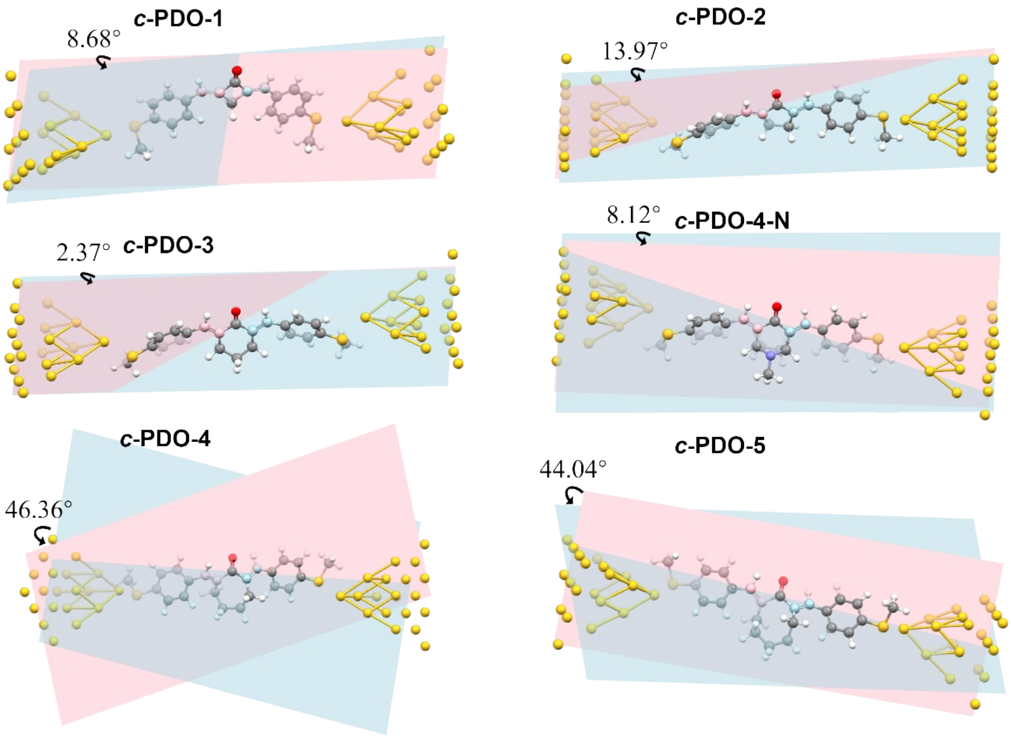


Fig. S10 Diagram of dihedral angles of ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4**, ***c*-PDO-4-N** and ***c*-PDO-5**.

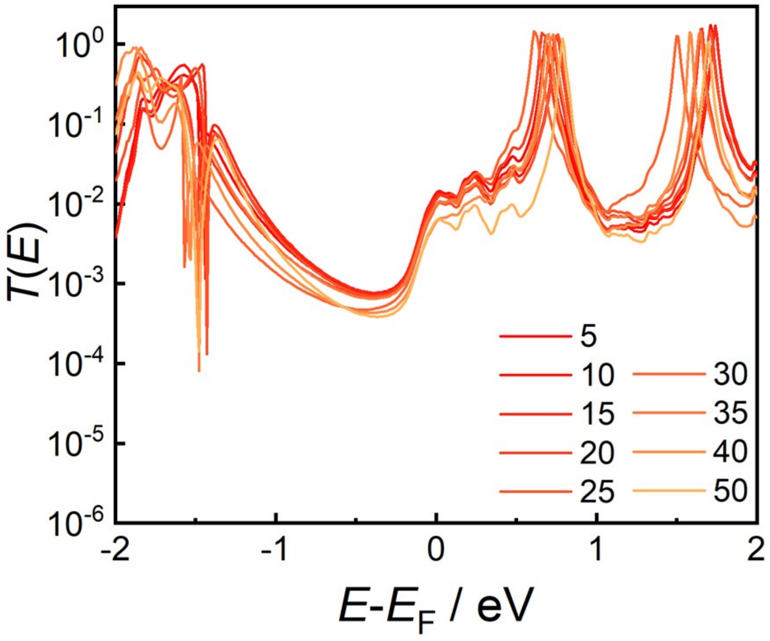


Fig. S11 Calculated $T(E)$ of **PDO-0** as the dihedron angels of the two vinyl groups are twisted from 5° to 50°.

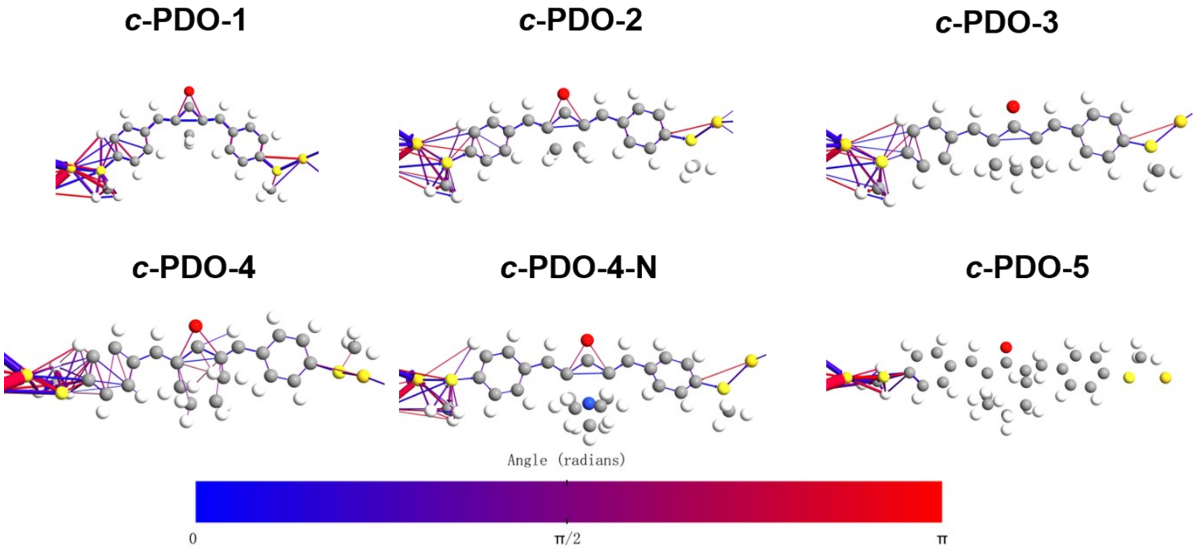


Fig. S12 The transmission pathways of ***c*-PDO-1**, ***c*-PDO-2**, ***c*-PDO-3**, ***c*-PDO-4**, ***c*-PDO-4-N** and ***c*-PDO-5** at the Fermi level (except the threshold of ***c*-PDO-4** is 0.0005, and the threshold of the remaining molecules is 0.005).

Table S3. Mulliken charges in CBs and ARs of each molecule.

	***c*-PDO-1**	***c*-PDO-2**	***c*-PDO-3**	***c*-PDO-4**	***c*-PDO-4-N**	***c*-PDO-5**
CB	-0.15	-0.58	-1.67	-2.05	-1.39	-1.97
AR	0.15	0.58	1.67	2.05	1.39	1.97

4. References

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