† Supplementary Data

Spirooxazine-based Multifunctional Molecular Switches with Tunable Photochromism and Nonlinear Optical Response

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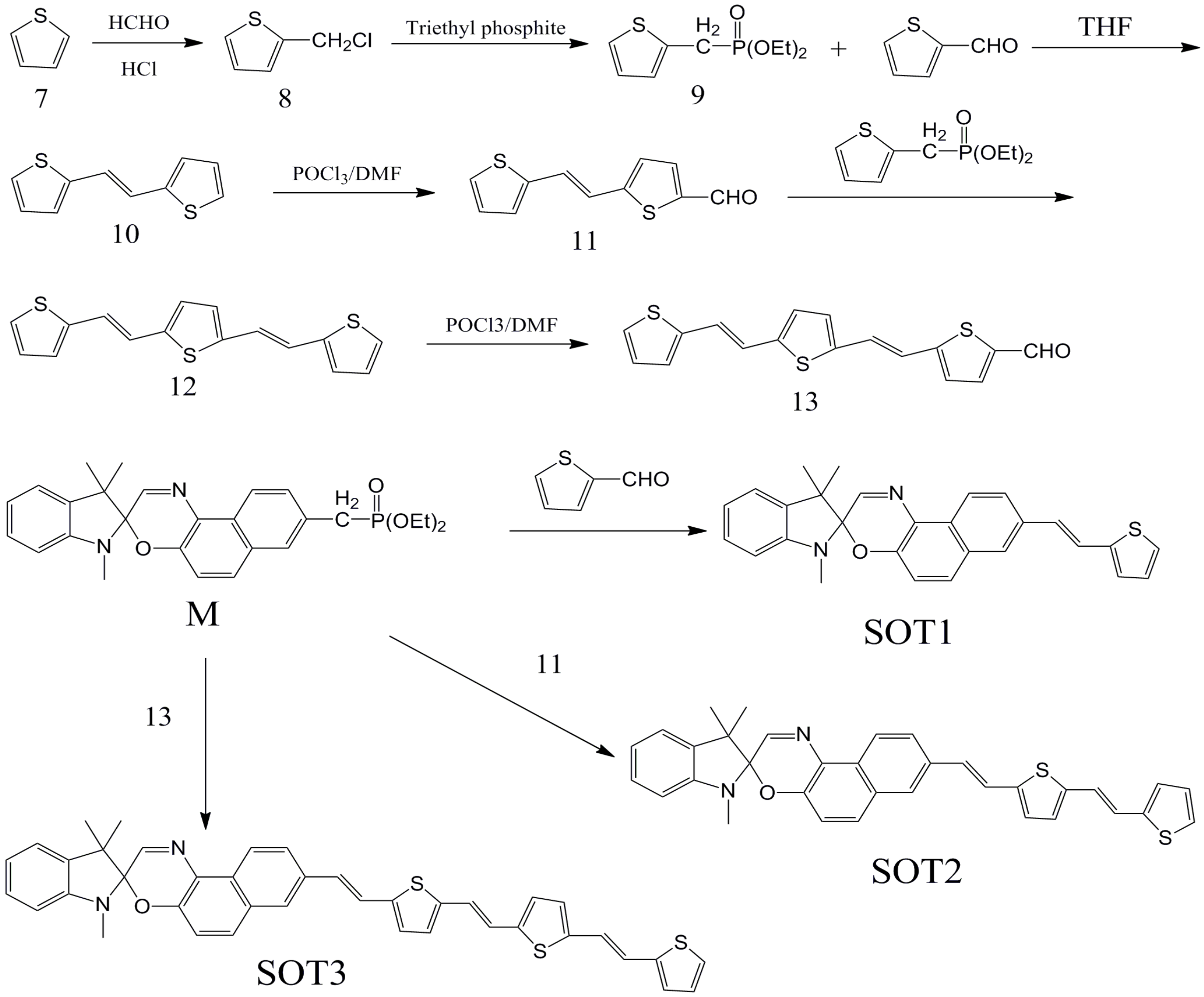
Experimental Section

Materials. 1,3,3-trimethyl-2-methyleneindoline was purchased from J&K and distilled to use. All other reagents were of analytical grade or Chemical purity and dried to use. Unless otherwise noted, all Solvents were dried and purified before used.



Scheme S1. Synthetic Routes to **SOT1, SOT2** and **SOT3.**

(E)-1,2-di(thiophen-2-yl)ethane (10)

Diethyl(thiophen-2-ylmethyl)phosphonate (2.3g, 10mmol) in the purified THF (40ml) were cooled under 0 °c using a salt bath. Thiophene-2-carbaldehyde (1.12g, 10mmol) in the purified THF (20ml) was slowly added to the solution during 30min. The mixture was gradually warmed to the room temperature and then refluxed for 3h. Saturated NaH solution were added to stop the reaction. The mixture was extracted with ether and washed with water. After dried with $MgSO_4$, the solution was rotary distilled to give a crude product and then recrystallized from cyclohexane ultimately resulting a pale yellow solid. Yield: 1.67g, 88%.

E-1-(2-aldehyde-5-thiophene)-2-(2-thienyl)ethylene (11)

Phosphorus oxychloride (3.83g, 25mmol) in the purified THF (20ml) were cooled under 0 °c using a salt bath and stirred for 1h. The resulting **10** (3.84g, 20mmol) in the purified THF (50ml) was slowly added to the solution during 1h under 0 °c. After that, The mixture was gradually warmed to 50℃ and then stirred for 3h. 50 ml water was added to stop the reaction. Organic phase was extracted with dichloromethane and washed with water. After dried with $MgSO_4$, the solution was rotary distilled to give a crude product and then recrystallized from cyclohexane ultimately resulting a pale yellow solid. Yield: 4.10g, 93%.

2,5-bis((E)-2-(thiophen-2-yl)vinyl)thiophene (12)

NaH (1.05g, 24mmol, 60%) in the purified THF (50ml) were cooled under 0 °c using a salt bath. 2-thiophene-methyl phosphate(5.6g, 24mmol) in the purified THF (10ml) was slowly added to the solution during 30min. And then the resulting **11** (4.4g, 20mmol) in the purified THF (50ml) was gradually added in the former solution and warmed to the room temperature and then refluxed for 3h. Hot water was added to stop the reaction. Solid was separated out from the solution and collected after the filtration. After washed with methanol and then dried, yellow solid was obtained. Yield: 5.29g, 88%.

E,E-2-[2-(5-aldehyde-2-thiophene)vinyl]-5-[2-(2-thiophene)vinyl] thiophene (13)

Phosphorus oxychloride (1.6g, 10mmol) in the purified THF (50ml) were cooled under 0 °c using a salt bath and stirred for 30 min. The resulting **12** (2.56g, 8.5mmol) in the purified THF (30ml) was slowly added to the solution during 1h under 0 °c. After that, The mixture was gradually warmed to 60℃ and then stirred for 5h. Water was added to stop the reaction. Organic phase was extracted with dichloromethane and washed with water. After filtered and purified by chromatography method using dichloromethane, it ultimately resulting a brownish yellow solid. Yield: 1.63g, 58%.

Table S1. (a) Selected B3LYP/6-31G(d) skeletal bond lengths and the bond length alternation (BLA) values for **SO-SOT3** and the corresponding open-forms.

bond	Length/Å										
	SO(expt[c])	O-SO	SOT1	O-SOT1	SOT2	O-SOT2	SOT3	O-SOT3	[b]O-SOT1	[b]O-SOT2	[b]O-SOT3
1	1.453(1.436)	1.371	1.453	1.370	1.453	1.370	1.452	1.370	1.383	1.385	1.387
2	1.514(1.504)	1.384	1.515	1.385	1.515	1.385	1.515	1.386	1.393	1.390	1.387
3	1.282(1.267)	1.352	1.281	1.351	1.281	1.350	1.281	1.350	1.342	1.343	1.344
4	1.400(1.417)	1.320	1.400	1.321	1.400	1.322	1.400	1.322	1.359	1.357	1.354
5	1.388(1.367)	1.496	1.388	1.496	1.388	1.497	1.388	1.497	1.468	1.470	1.473
6	1.361(1.362)	1.242	1.360	1.241	1.360	1.241	1.359	1.241	1.259	1.258	1.257
7	1.460(1.454)	-	1.461	-	1.462	-	1.462	-	-	-	-
8	1.431(1.425)	1.474	1.429	1.470	1.429	1.469	1.429	1.469	1.446	1.447	1.449
9	1.432(1.410)	1.421	1.433	1.423	1.433	1.423	1.433	1.424	1.447	1.444	1.441
10	1.419(1.412)	1.407	1.413	1.400	1.413	1.400	1.413	1.400	1.396	1.397	1.398
11	1.377(1.363)	1.388	1.391	1.402	1.391	1.403	1.391	1.403	1.406	1.405	1.403
BLA[a]	-	0.023	-	0.015	-	0.014	-	0.0137	-0.0098	-0.006	-0.0018

[a] The BLA values: (R1 + R3 + R8 + R10)/4 - (R2 + R4 + R9 + R11)/4.

[b] Optimization of first singlet excited state S_1 by TD-B3LYP/6-31(d).

[c] Millini, R.; Del Piero, G.; Allegrini, P.; Crisci, L.; Malatesta, V. *Acta Crystallogr.* C 1991, 47, 2567.

Table S1. (b) Selected B3LYP/6-31G(d) skeletal bond lengths and the bond length alternation (BLA) values for O-SOT1 in different solvents.[d]

bond	Length/Å								
Solvent	Gas	CH_3Cl	CH_2Cl_2	Acetone	Methanol	Acetonitrile	Water	Formamide	nMFM[c]
ϵ[b]	1.0	4.711	8.93	20.49	24.85	35.69	78.36	108.9	181.6
1	1.370	1.362	1.360	1.359	1.359	1.359	1.358	1.358	1.358
2	1.385	1.393	1.395	1.396	1.397	1.397	1.397	1.397	1.397
3	1.351	1.344	1.342	1.341	1.341	1.341	1.340	1.340	1.340
4	1.321	1.327	1.329	1.330	1.330	1.330	1.331	1.331	1.331
5	1.496	1.489	1.487	1.485	1.485	1.485	1.485	1.485	1.485
6	1.241	1.247	1.248	1.249	1.249	1.249	1.250	1.250	1.250
8	1.470	1.468	1.467	1.467	1.467	1.467	1.467	1.467	1.467
9	1.423	1.424	1.424	1.425	1.425	1.425	1.425	1.425	1.425
10	1.400	1.402	1.402	1.402	1.403	1.403	1.403	1.403	1.403
11	1.402	1.402	1.401	1.401	1.401	1.401	1.401	1.401	1.401
BLA[a]	0.0150	0.0075	0.0055	0.0043	0.0043	0.0043	0.0035	0.0035	0.0035
DM[d]	3.15	5.11	5.57	5.91	6.02	6.04	6.13	6.16	6.18
“O”[e]	-	-0.572	-0.580	-0.585	-0.587	-0.587	-0.588	-0.589	-0.589

[a] The BLA values :(R1 + R3 + R8 + R10)/4 - (R2 + R4 + R9 + R11)/4.

[b] Dielectric constant, ϵ, and represents the solute by means of cavity built with a number of interlaced spheres. [c] n-MethylFormamide-Mixture (nMFM). [d] Dipole Moment. [e] Mulliken

atomic charge on oxygen atoms. [d] Geometry optimization by B3LYP/6-31G(d) with polarizable continuum model (PCM).

Table S1. (c) Annihilation of the spin contaminant for the open forms of SOT1-SOT3.

	Open-shell Singlet State		Open-shell Triplet State	
Compounds	Before	After	Before	After
O-SOT1	0.0234	**0.0001**	2.0293	**2.0005**
O-SOT2	0.0253	**0.0001**	2.0349	**2.0007**
O-SOT3	0.0266	**0.0001**	2.0370	**2.0008**

Table S1. (d) The calculated total energies (in a.u.) for the open forms of SOT1-SOT3 at R/U-B3LYP/6-31G(d) level.

Compounds	Close-shell Singlet	Open-shell Singlet	Open-shell Triplet
O-SOT1	-1664.32928	-1664.31180	-1664.29263
O-SOT2	-2293.54900	-2293.53154	-2293.51257
O-SOT3	-2922.77250	-2922.75592	-2922.73619

Table S2. Calculated electronic absorption energies (λ_{cal}, ΔE) of **SOT1-SOT3** and the corresponding open-forms in $CHCl_3$ solvent using B3LYP/6-31+G(d) and CAM-B3LYP/6-31+G(d).

Compd	Exp nm (eV)	B3LYP nm (eV)	CAM-B3LYP nm (eV)
SOT1	356 (3.48)	414 (3.00)	360 (3.44)
SOT2	418 (2.97)	503 (2.03)	437 (2.84)
SOT3	456 (2.72)	587 (2.11)	494 (2.51)
O-SOT1	590 (2.10)	588 (2.11)	518 (2.39)
O-SOT2	610 (2.03)	646 (1.92)	531 (2.33)
O-SOT3	625 (1.98)	686 (1.81)	543 (2.28)

Table S3. Redox Potentials (V vs SCE) for SOT1-SOT3 in CH_3CN at ~300 K[a]

Compd	E_{pa}^{1} (V)[a]	E_{pa}^{2}(V)	E_{pr}^{1}(V)	E_{pr}^{2}(V)	E_{pr}^{3}(V)
SOT1	-0.68	0.84	-1.01	-1.91	-
SOT2	-0.66	0.75	-1.07	-1.85	-
SOT3	-0.62	0.69	-1.12	-1.84	-1.66

[a] Experimental conditions: electrolyte, 0.1M TBAP in deoxygenated CH_3CN solution; scan rate, 100 mV/s; electrode configuration, glassy carbon working electrode, silver pseudoreference electrode, platinum counter electrode; versus SCE.

Table S4. The atomic charge distribution of SOT1-SOT3 on the ground state S_0 as deduced from the Natural Population Analysis (NPA).

	Natural Population Analysis (NPA) (e)		
SOT1	0.295	-0.311	0.016
SOT2	0.295	-0.309	0.014
SOT3	0.296	-0.306	0.010

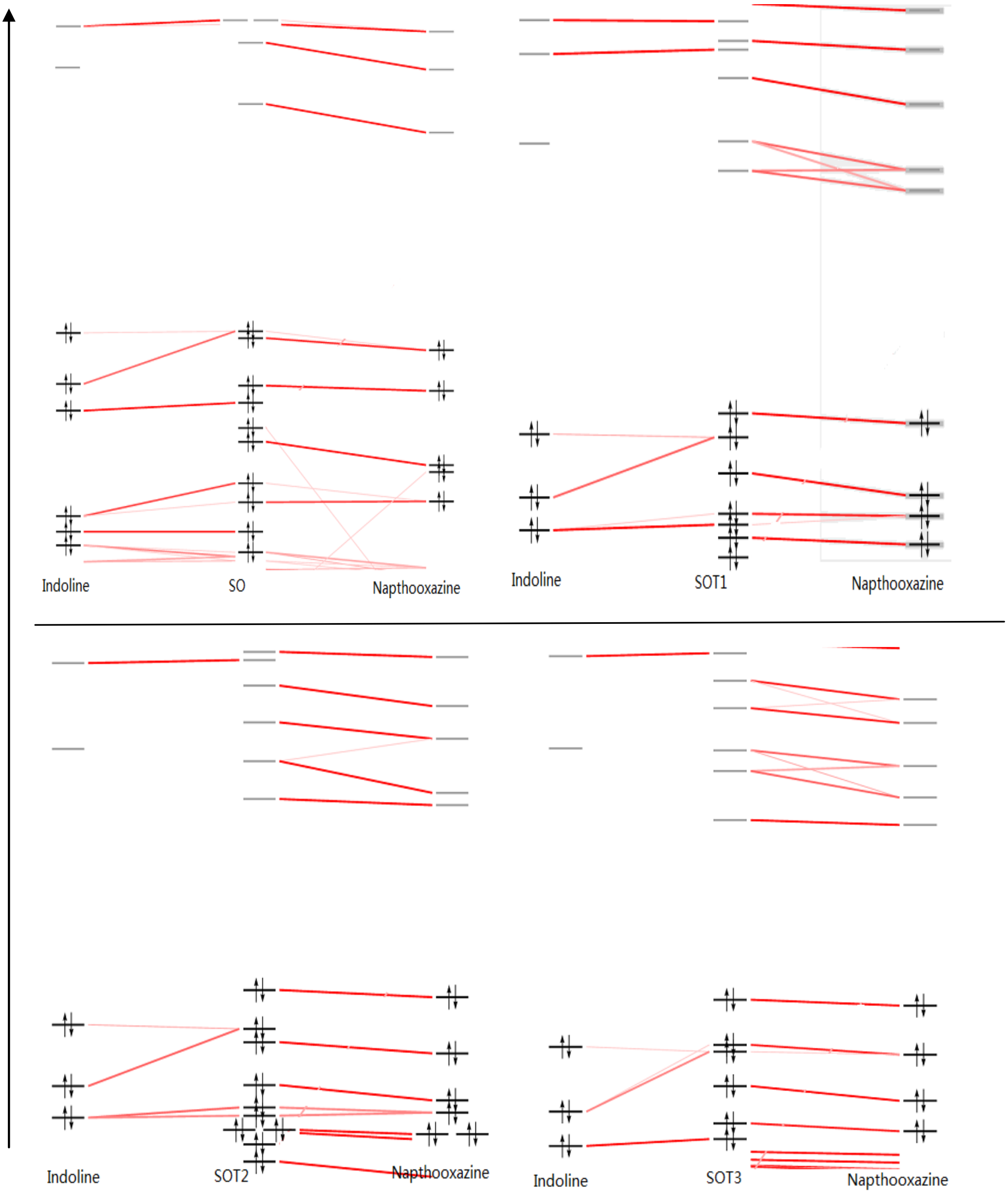


Fig. S1. Diagram of interactions between frontier molecular orbitals of indoline, naphthoxazine, and their spiro form. SO(top, left), SOT1(top, right), SOT2(bottom, left) and SOT3(bottom, right). The interaction plots are calculated and plotted by the graphical user interface of Amsterdam Density Functional Package.

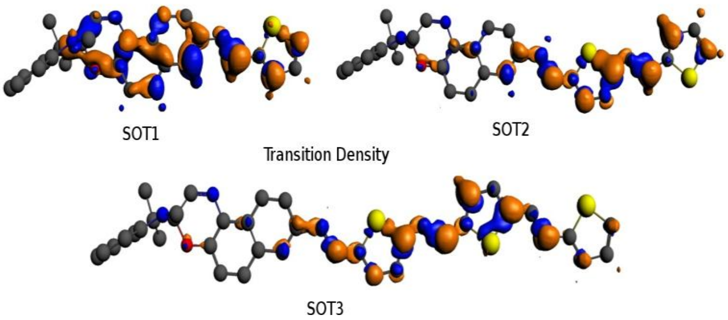


Fig. S2 Plot of transition density for the corresponding first singlet states of **SOT1-SOT3** where golden color indicates the charge decrease and blue color indicates the charge increase.

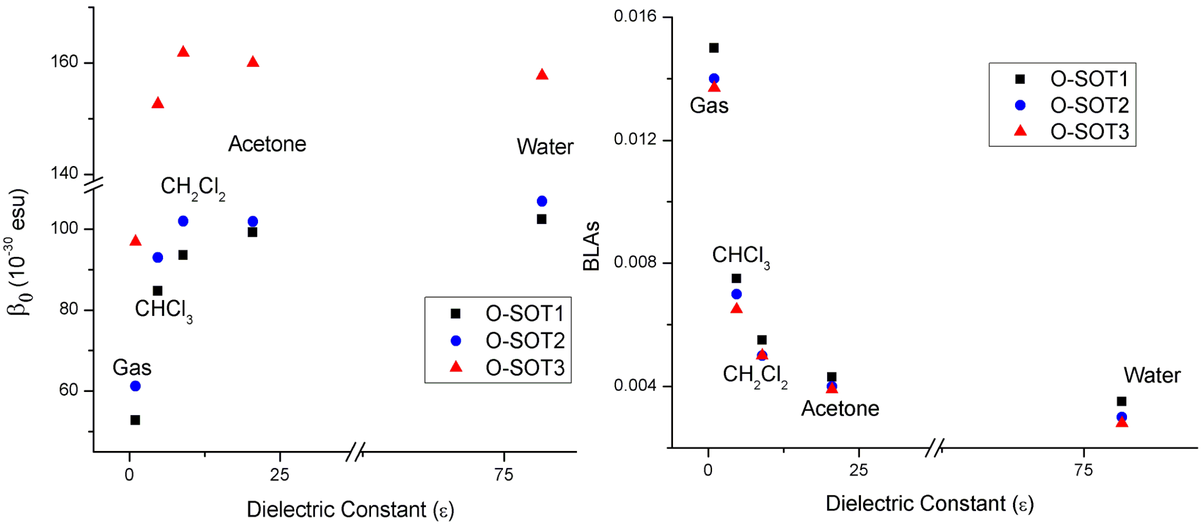
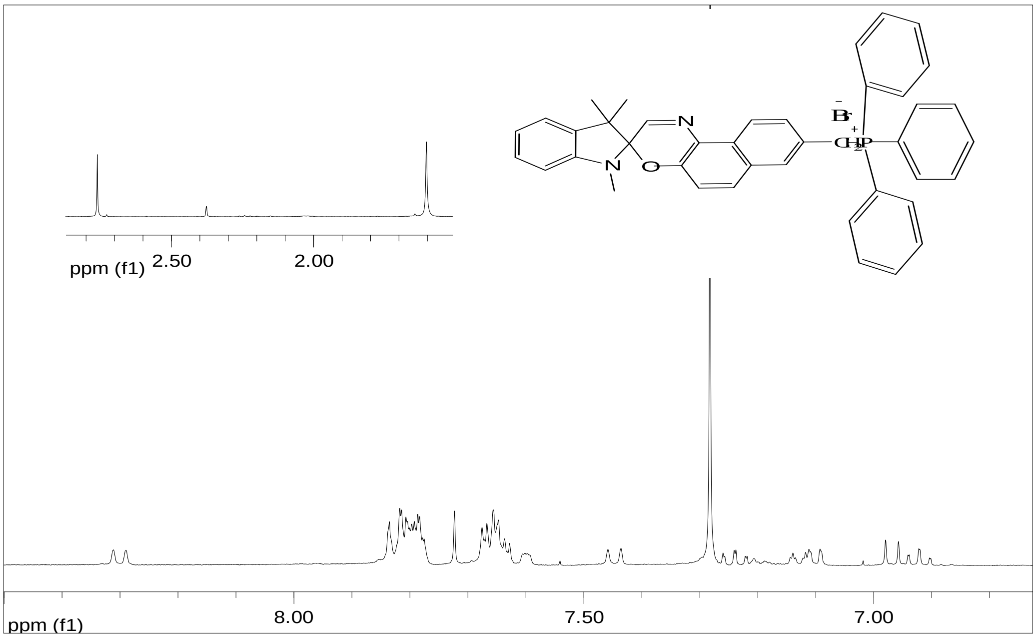
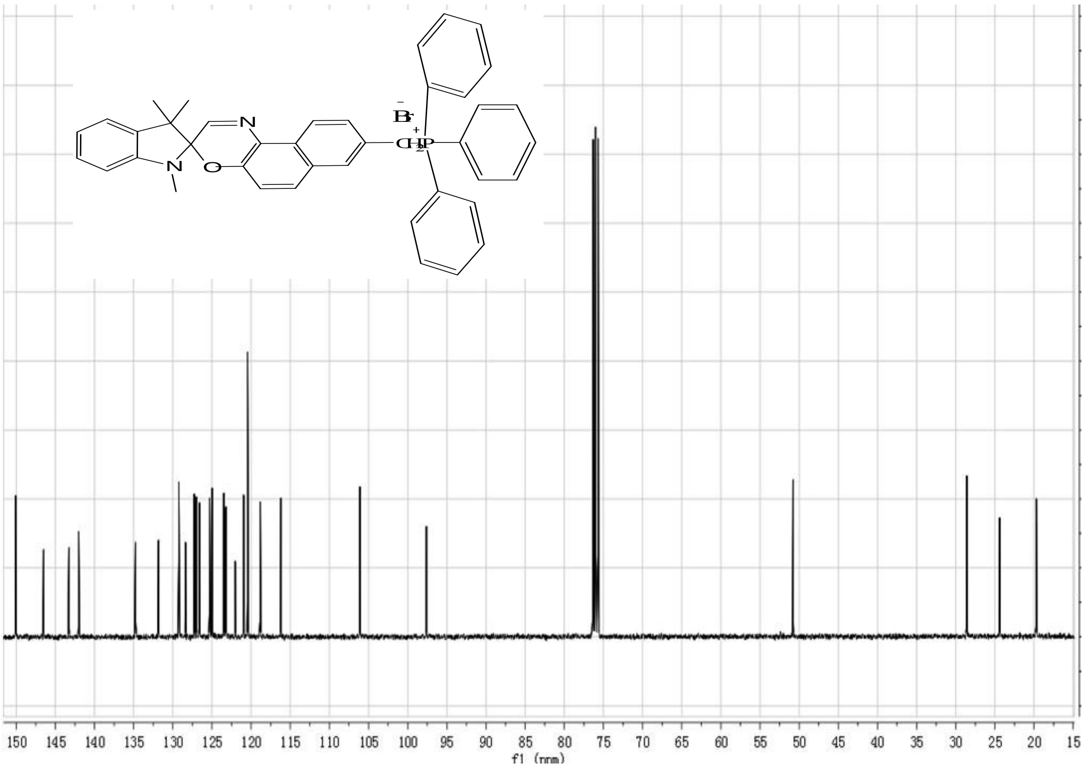


Fig.S3 Calculated static β values (10^{-30} esu) versus solvent polarity (left), Calculated BLA versus solvent polarity (right).

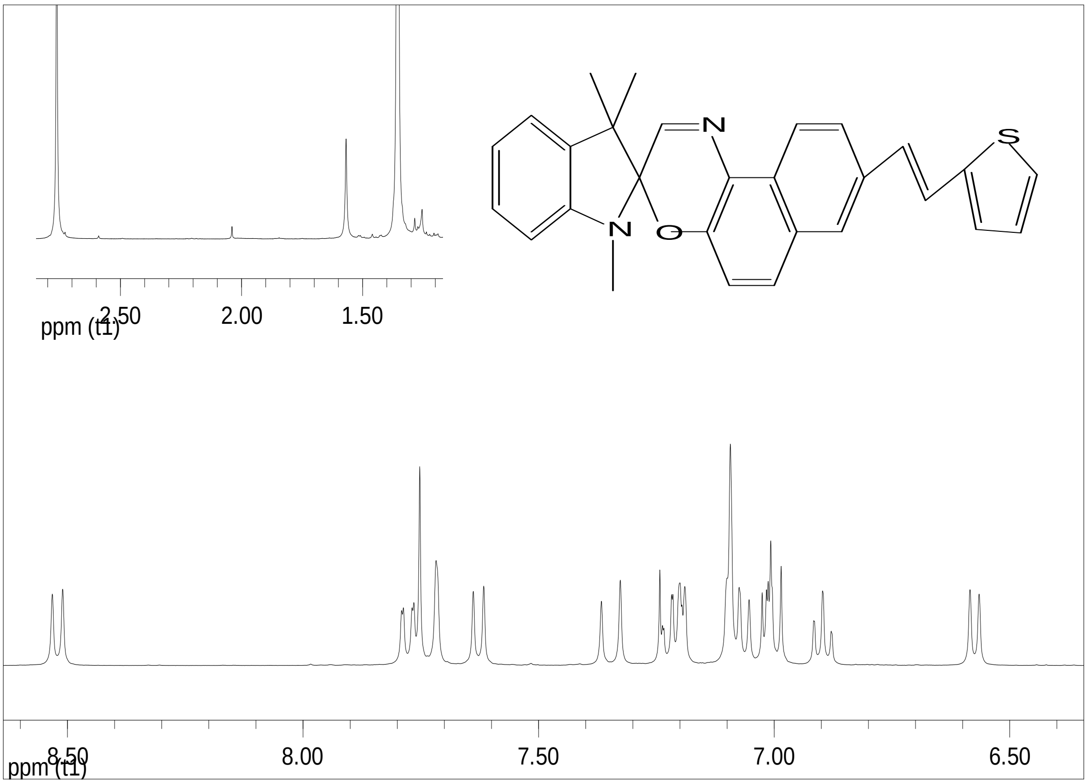
Characterization Data for Products (including ^{1}H NMR and ^{13}C NMR Spectra and MS spectrum)

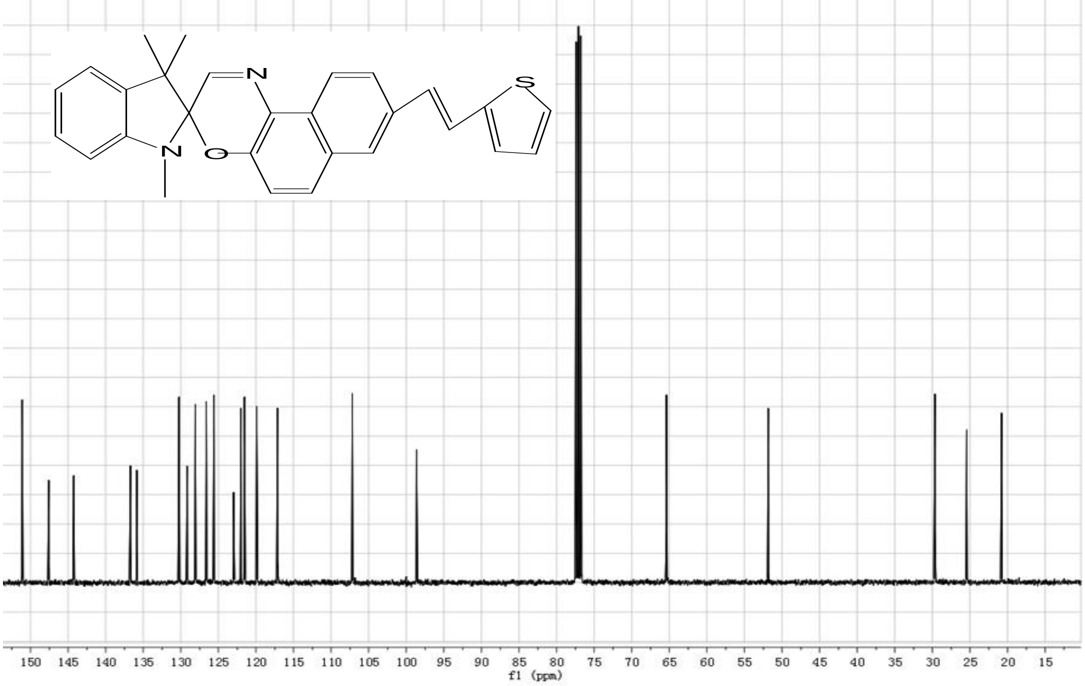
^{1}H and ^{13}C NMR Spectra for **M**



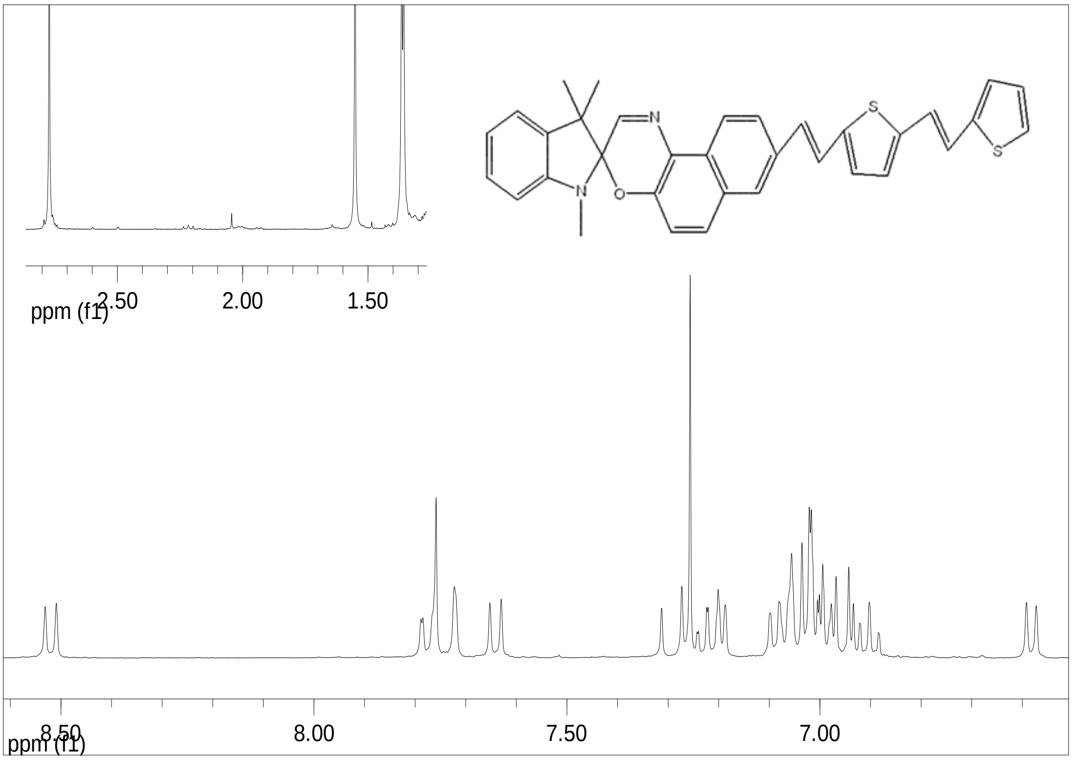


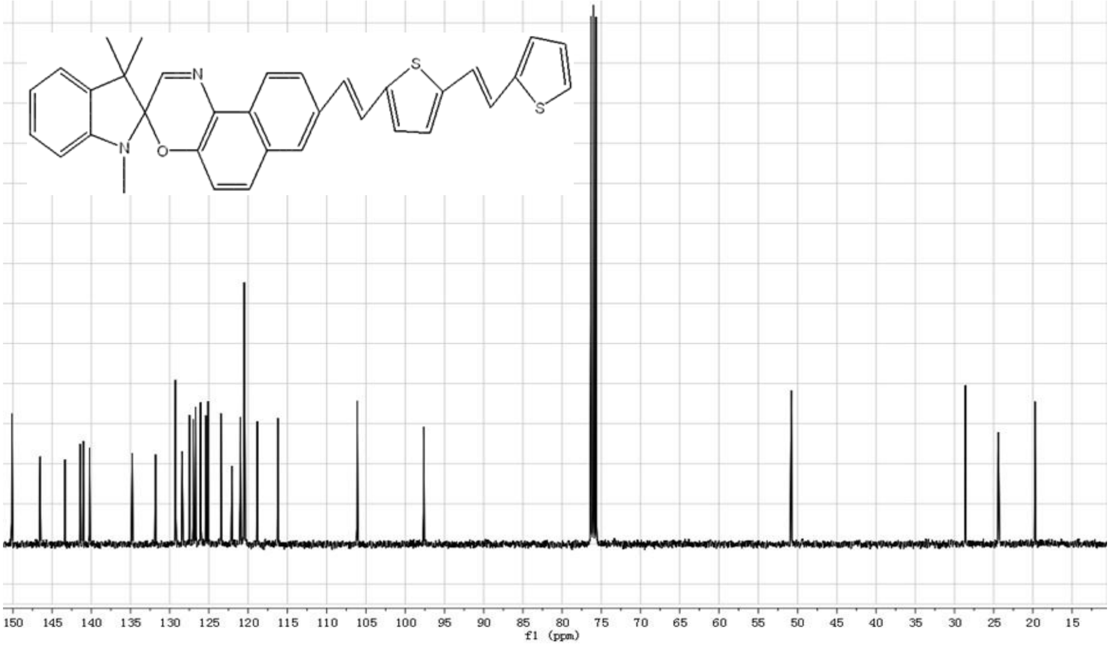
^{1}H and ^{13}C NMR Spectra **for SOT1**



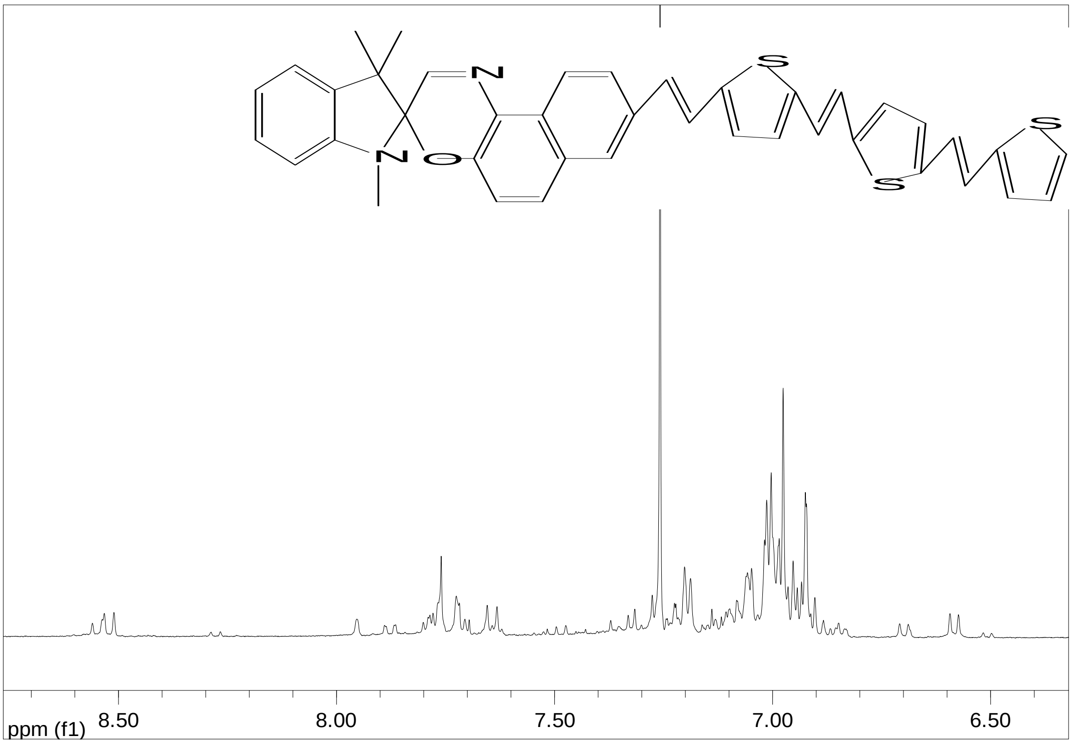


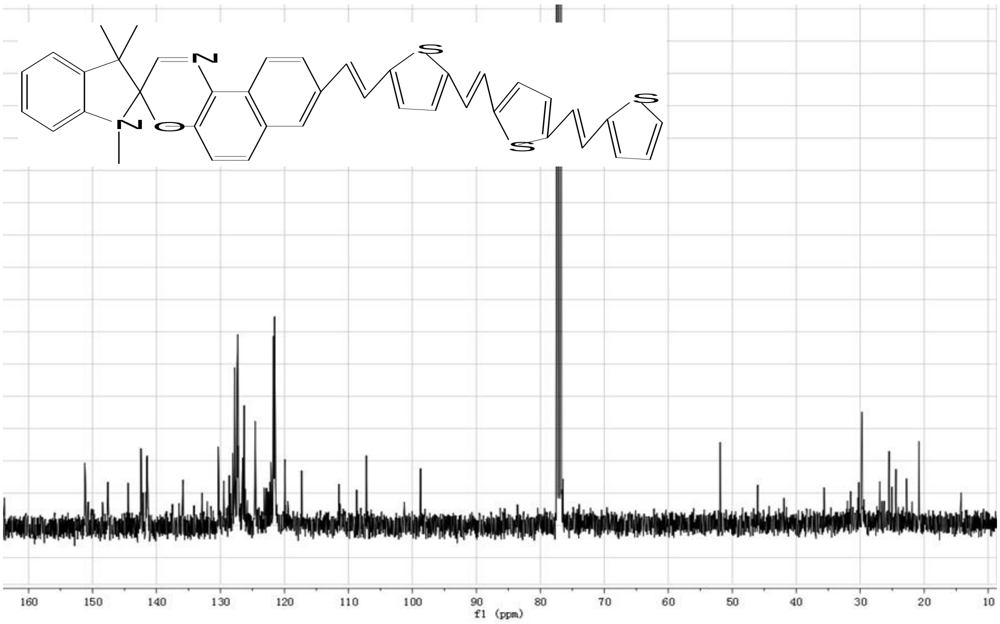
^{1}H and ^{13}C NMR Spectra for **SOT2**





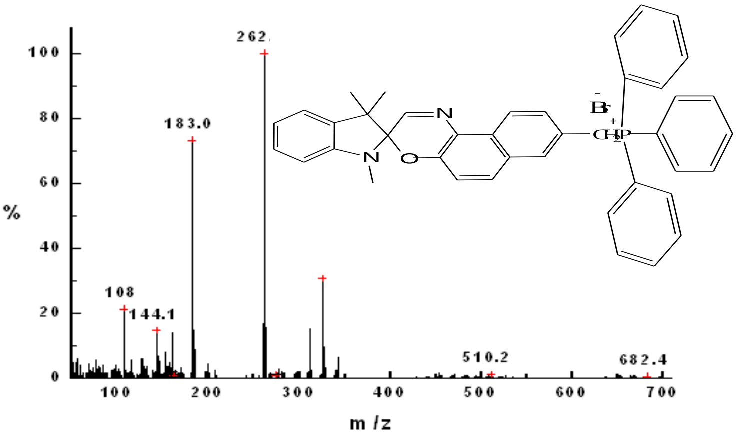
^{1}H and ^{13}C NMR Spectra for **SOT3**



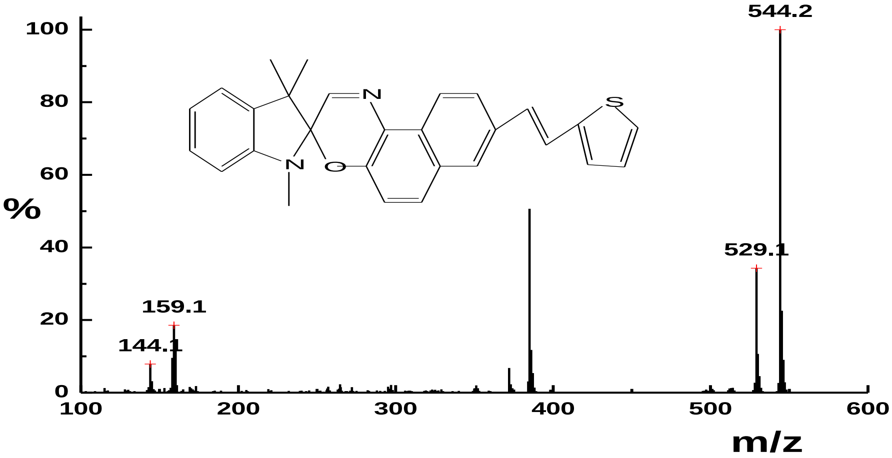


MS Spectra for **M** , **SOT1, SOT2** and **SOT3**

M



SOT1



SOT2

SOT3