

## SUPPORTING INFORMATION

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### Supporting Information

#### **Designing a near-infrared circularly polarized luminescent dye by dissymmetric spiro-fusion**

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### 1. Materials and Methods

**Materials.** All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified.

**Characterizations of compounds.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained in deuterated solvents on a Bruker ADVANCE 500 NMR Spectrometer. Chemical shifts are expressed in ppm using the residual protonated solvent as an internal standard. The signals have been named as follows: s (singlet), d (doublet), and m (multiplets). High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer.

**Optical characterizations.** UV-vis absorption spectra were measured with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1 cm quartz cell.

**Electrochemical characterizations.** Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation, with glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mV/s. 0.1 M tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) dissolved in  $\text{CH}_2\text{Cl}_2$  (HPLC grade) was used as the supporting electrolyte, which was calibrated by the redox couple of ferrocene/ferricenium ( $\text{Fc}/\text{Fc}^+$ ).

### 2. Synthesis and Characterization

The starting material monobrominated TDI (**1**) was synthesized according to literature procedures.<sup>[1]</sup>

**SDT:** a Schlenk flash was charged with monobrominated TDI (**1**) (200 mg, 0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (45 mg, 0.2 mmol),  $\text{KHCO}_3$  (160 mg, 1.6 mmol), and  $\text{KOAc}$  (176 mg, 1.8 mmol) under argon. Then 1,4-dioxane (10 mL),  $\text{CH}_2\text{Br}_2$  (0.1 mL, 1.4 mmol) and *i*-PrOH (30  $\mu\text{L}$ , 0.4 mmol) were adding by injection, and the reaction mixture was heated to 75  $^\circ\text{C}$  for 6 h. After cooling down and removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether / $\text{CH}_2\text{Cl}_2$ , 1:1 v/v) to yield dark blue solid **SDT** (103 mg, 55%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_2\text{CDCl}_2$ , 373 K):  $\delta$  = 8.78-8.73 (m, 6H), 8.67-8.62 (m, 6H), 8.34-8.33 (d,  $J$  = 8.2 Hz, 2H), 8.20-8.18 (d,  $J$  = 9.5 Hz, 4H), 8.06 (s, 2H), 5.10-5.06 (m, 4H), 2.17-2.12 (m, 8H), 1.86-1.81 (m, 8H), 1.28-1.18 (m, 80H), 0.82-0.76 (m, 24H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_2\text{CDCl}_2$ , 373 K):  $\delta$  = 164.04, 142.74, 141.47, 138.73, 138.53, 136.37, 136.17, 134.76, 132.95, 132.66, 132.07, 131.71, 131.35, 131.06, 130.18, 129.94, 129.02, 126.77, 126.50, 126.10, 125.94, 125.03, 123.60, 123.15, 122.82, 122.48, 121.75, 119.31, 54.86, 54.77, 32.61, 32.51, 31.66, 29.38, 29.02, 28.97, 26.96, 22.41, 22.39, 13.80; HRMS (MALDI, 100%): calcd (%) for  $\text{C}_{129}\text{H}_{144}\text{N}_4\text{O}_8$ : 1877.0989; found, 1877.0983. The specific rotation of S-(+)-**SDT** (>98% ee) showed  $[\alpha]_{25}^{436}$  of + 2565 ( $c$  = 0.001,  $\text{CH}_2\text{Cl}_2$ ).

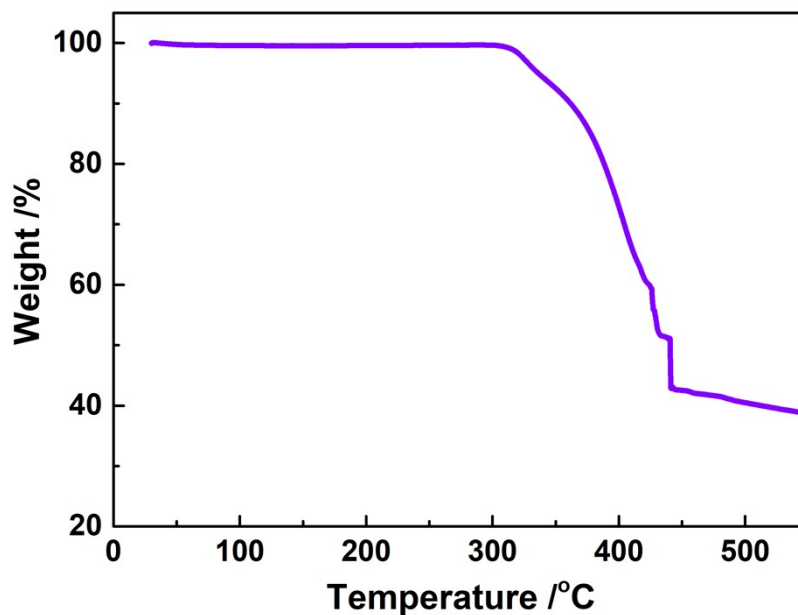


Fig. S1 The TGA plot of SDT.

### 3. Computational Details

Due to the little effect of the alkyl-branched chain on electronic structures and optical properties, all the alkyl chain was replaced by the methyl groups during calculation. All the ground state geometry optimization was performed using density functional theory (DFT) at the B3LYP/6-31G (d) level. The calculation of absorption spectrum and electronic circular dichroism (ECD) was calculated by Time-dependent density functional theory (TD-DFT) at the BMK/6-31G (d) level given the effect of the solvent (dichloromethane) within polarizable continuum model (PCM) in a linear response. All the above calculations were carried out by the aid of Gaussian 09 software package.<sup>[2]</sup>

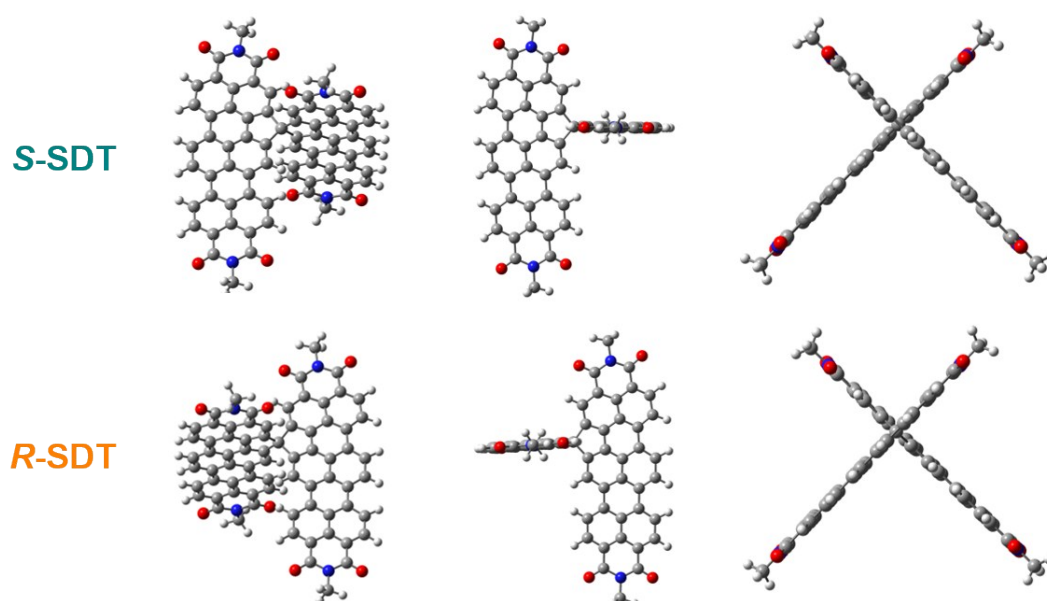
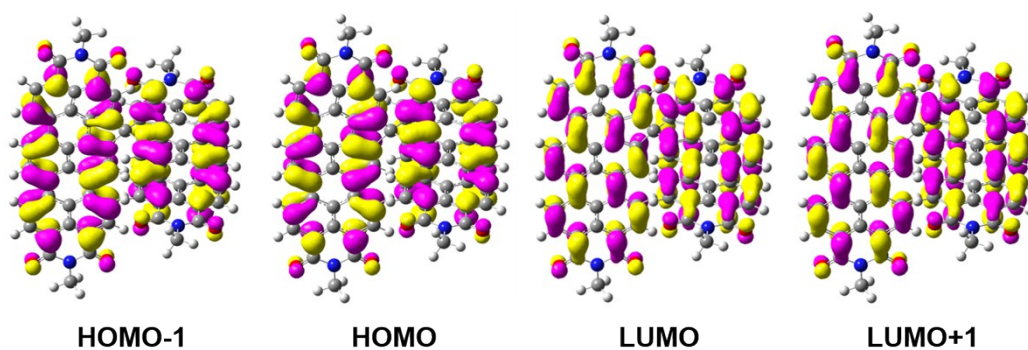


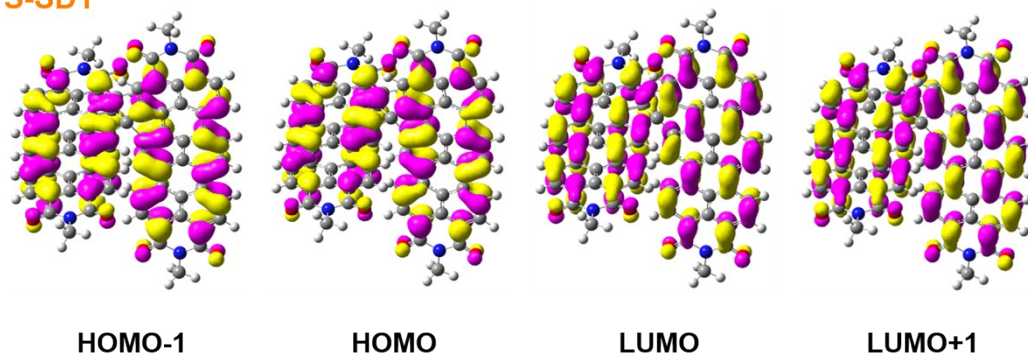
Fig. S2 Optimized geometries of *R*-SDT and *S*-SDT by DFT at the B3LYP/6-31G(d) level.

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### R-SDT



### S-SDT



**Fig. S3** Optimized frontier orbitals of **R-SDT** and **S-SDT** by DFT at the B3LYP/6-31G(d) level.

**Table S1** Eigenvector components of the TD-DFT eigenstates for **R-SDT** and **S-SDT** with the highest oscillator strength  $f$ .

#### **R-SDT (HOMO: Orbital 281)**

Excited State 1:	Singlet-A	1.9674 eV	630.20 nm	$f=1.1719$	$\langle S^{*2} \rangle = 0.000$
	280 -> 283	0.28795			
	281 -> 282	0.64294			
Excited State 2:	Singlet-A	1.9852 eV	624.53 nm	$f=1.1307$	$\langle S^{*2} \rangle = 0.000$
	280 -> 282	0.26643			
	281 -> 283	0.65202			
Excited State 3:	Singlet-A	2.2248 eV	557.29 nm	$f=0.2112$	$\langle S^{*2} \rangle = 0.000$
	280 -> 283	0.64166			
	281 -> 282	-0.28556			
Excited State 4:	Singlet-A	2.2289 eV	556.26 nm	$f=0.2438$	$\langle S^{*2} \rangle = 0.000$
	280 -> 282	0.65125			
	281 -> 283	-0.26380			

#### **S-SDT (HOMO: Orbital 281)**

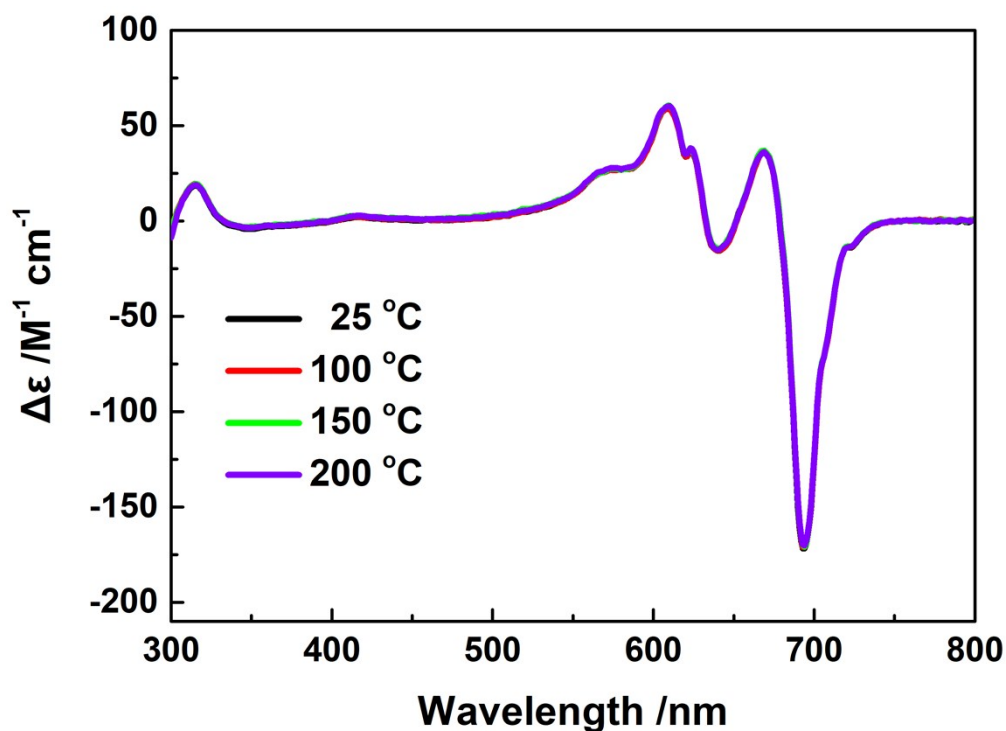
Excited State 1:	Singlet-A	1.9672 eV	630.26 nm	$f=1.1714$	$\langle S^{*2} \rangle = 0.000$
	280 -> 283	-0.28322			
	281 -> 282	0.63435			
	281 -> 283	0.10556			

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Excited State 2:	Singlet-A	1.9851 eV	624.59 nm	f=1.1302	<S**2>=0.000
280 -> 282		-0.26197			
281 -> 282		-0.10751			
281 -> 283		0.64317			
Excited State 3:	Singlet-A	2.2247 eV	557.30 nm	f=0.2117	<S**2>=0.000
280 -> 283		0.63753			
281 -> 282		0.27809			
Excited State 4:	Singlet-A	2.2289 eV	556.27 nm	f=0.2438	<S**2>=0.000
280 -> 282		0.64689			
281 -> 283		0.25668			

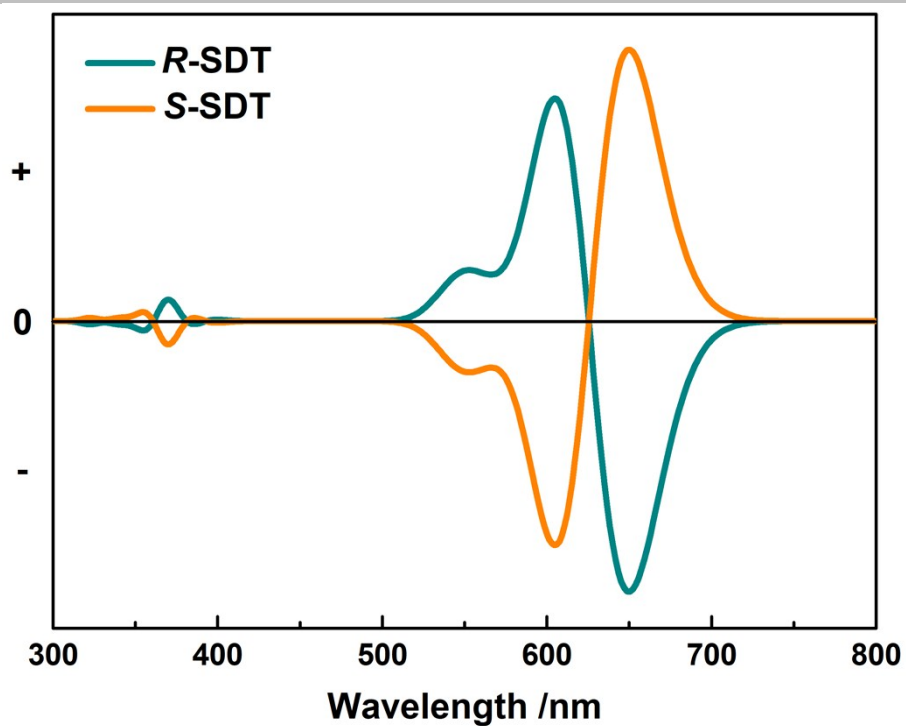
### 4. Chiroptical Properties

Absorption spectra with different concentrations and in film were measured with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1 mm quartz cell or a quartz plate.

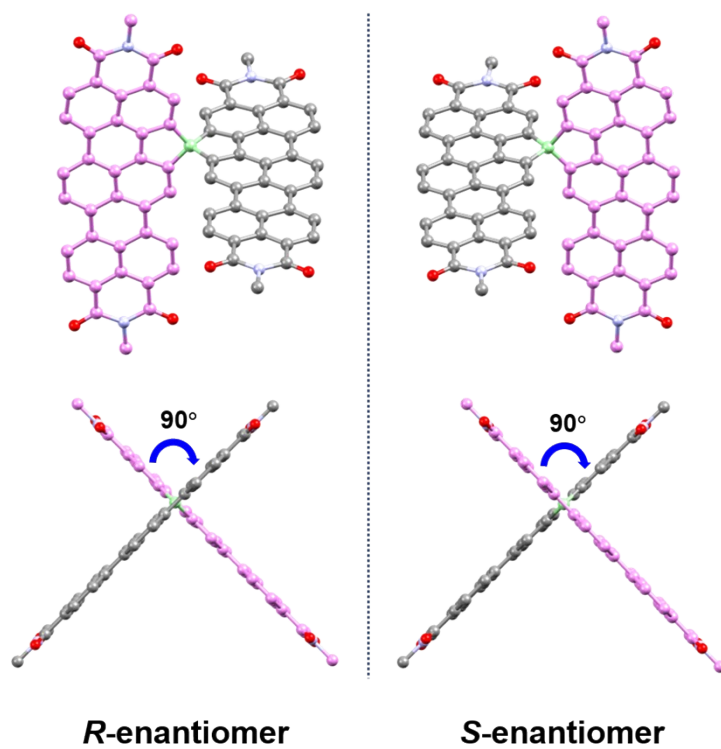


**Fig. S4** CD spectra of the first fraction of **SDT** after heating at different temperatures for 6 h.

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**Fig. S5** B3LYP/6-31G computed CD spectra of the *R*-enantiomer (dark cyan trace) and *S*-enantiomer (orange trace).



**Fig. S6** B3LYP/6-31G computed CD spectra of the *R*-enantiomer (dark cyan trace) and *S*-enantiomer (orange trace).

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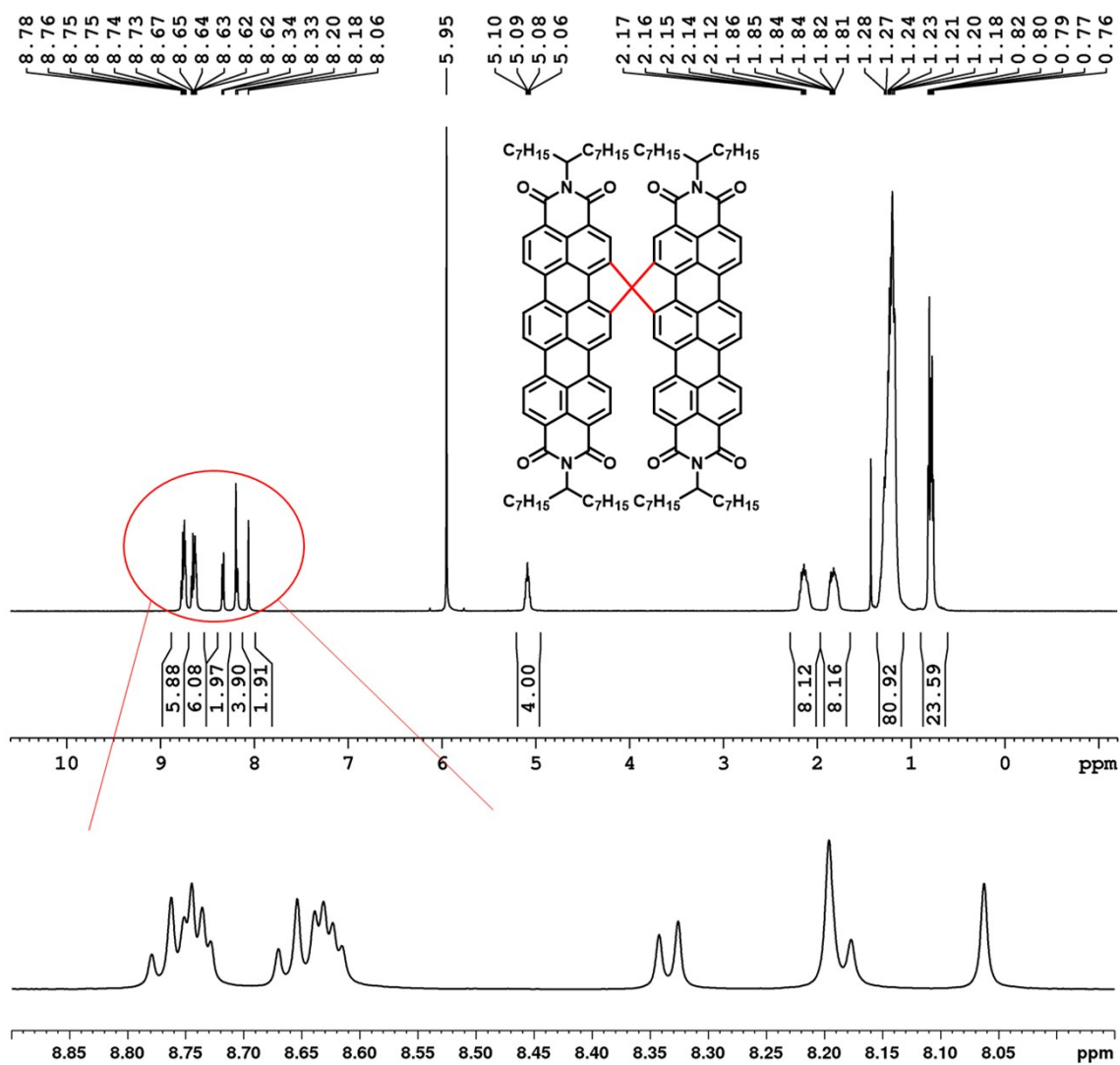
### 5. References

- [1] J. Feng, N. Liang, W. Jiang, D. Meng, R. Xin, B. Xu, J. Zhang, Z. Wei, J. Hou, and Z. Wang, *Org. Chem. Front.*, 2017, **4**, 811-816.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2013.

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## 6. NMR and HRMS Spectra

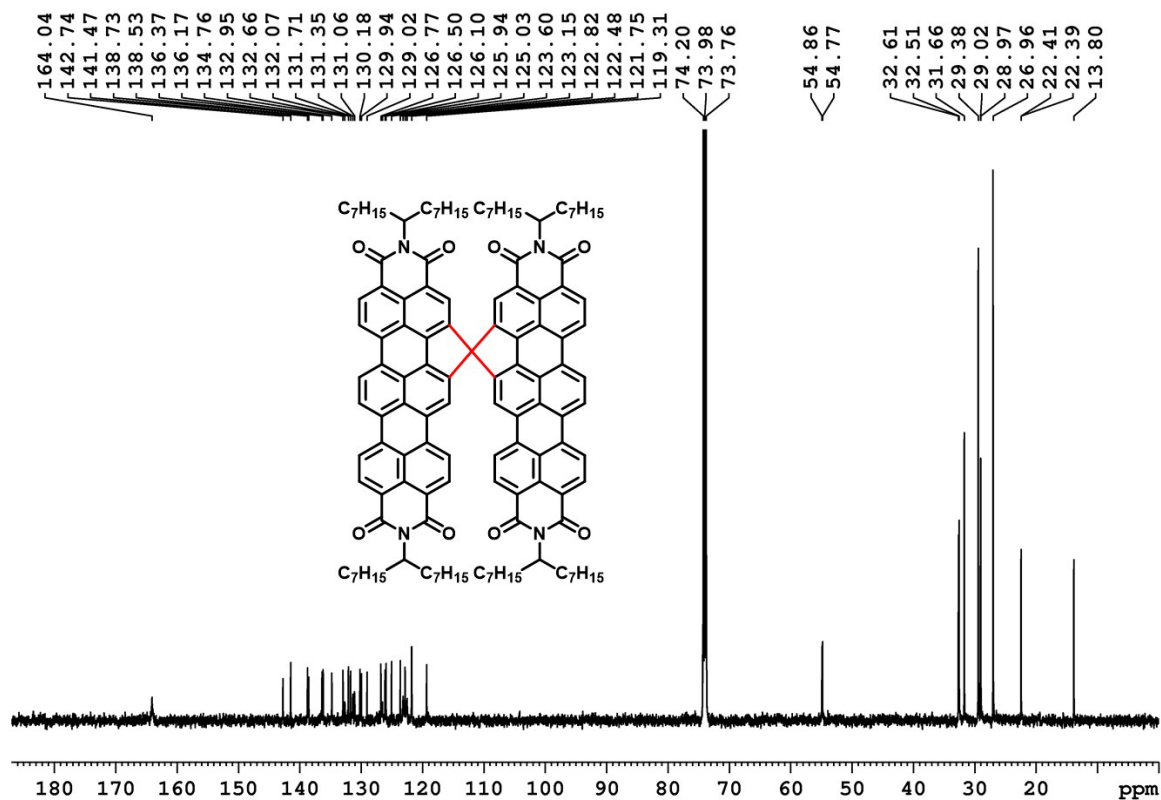
$^1\text{H}$  NMR spectrum of **SDT** in  $\text{CDCl}_2\text{CDCl}_2$  (373 K)





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$^{13}\text{C}$  NMR spectrum of **SDT** in  $\text{CDCl}_2\text{CDCl}_2$  (373 K)



HRMS (MALDI) of **SDT**

