Electronic Supplementary Information (ESI)

Invisible photochromism and optical anti-counterfeiting based on D-A type inverse diarylethene

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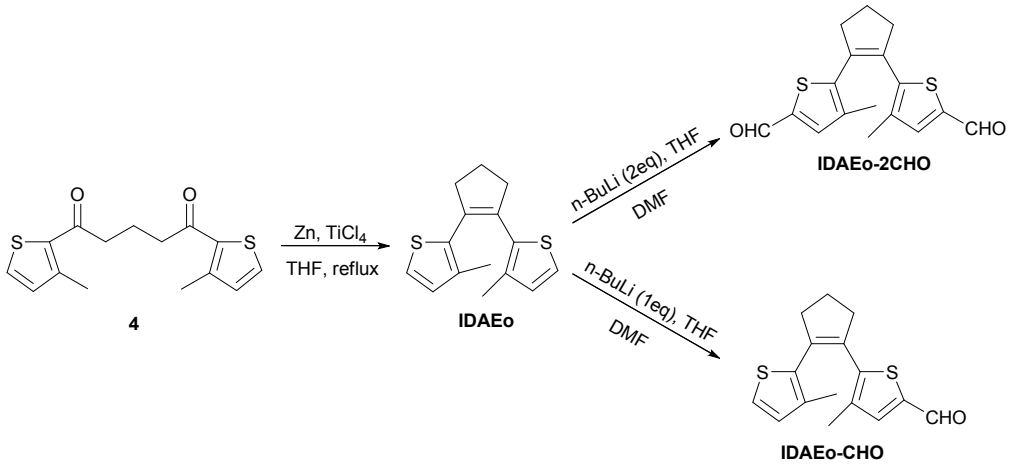


Scheme S1 Synthetic routine of compounds **IDAEo**, **IDAEo-2CHO** and **IDAEo-CHO**.

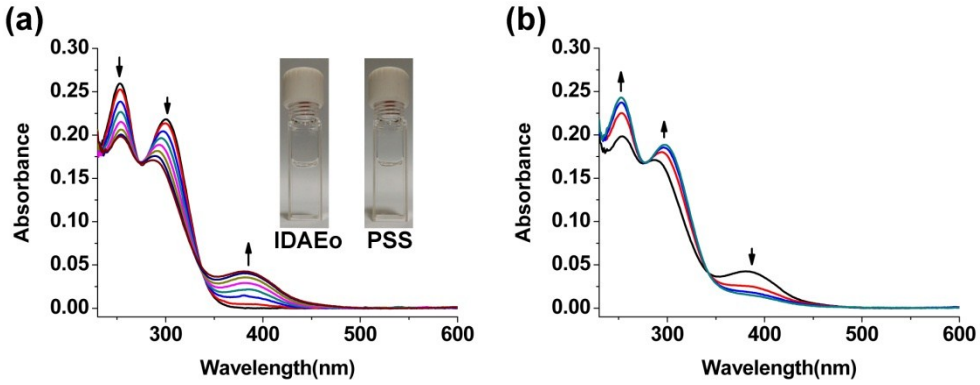


Fig. S1 (a) Absorption spectral changes of **IDAEo** (1.0×10^{-5} M) upon irradiation with 254 nm light in CH_2Cl_2. (b) Absorption spectral changes of PSS (1.0×10^{-5} M) upon irradiation with 365 nm light in CH_2Cl_2. Insets in (a): photographs of color changes of **IDAEo** before (left) and after (right) irradiation with 254 nm light.

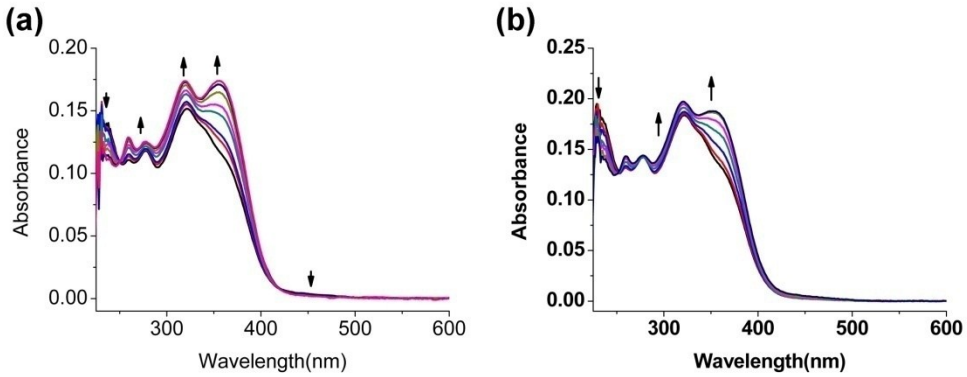


Fig. S2 (a) Absorption spectral changes of PSS of **IDAE-2CHO** (0.8×10^{-5} M) upon irradiation with >420 nm light in CH_2Cl_2. (b) Absorption spectral changes of PSS of **IDAE-2CHO** (1.0×10^{-5} M) upon irradiation with 254 nm light in CH_2Cl_2.

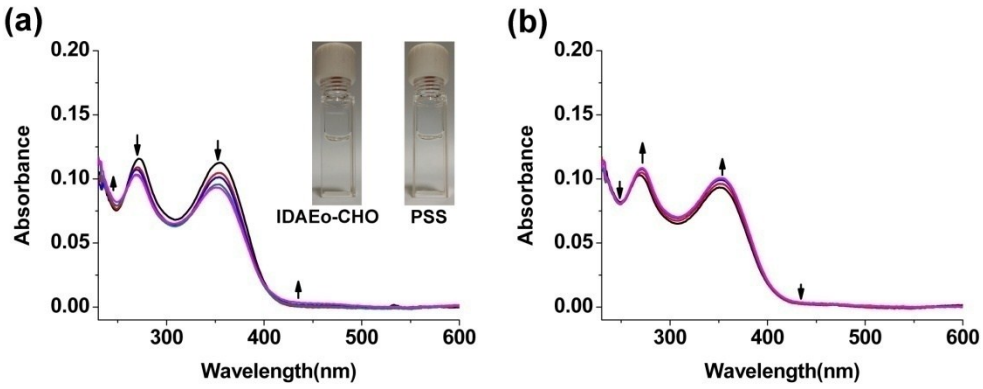


Fig. S3 (a) Absorption spectral changes of **IDAEo-CHO** (1.0×10^{-5} M) upon irradiation with 365 nm light in CH_2Cl_2. (b) Absorption spectral changes of PSS (1.0×10^{-5} M) upon irradiation with >420 nm light in CH_2Cl_2. Insets in (a): photographs of color changes of **IDAEo-CHO** before (left) and after (right) irradiation with 365 nm light.

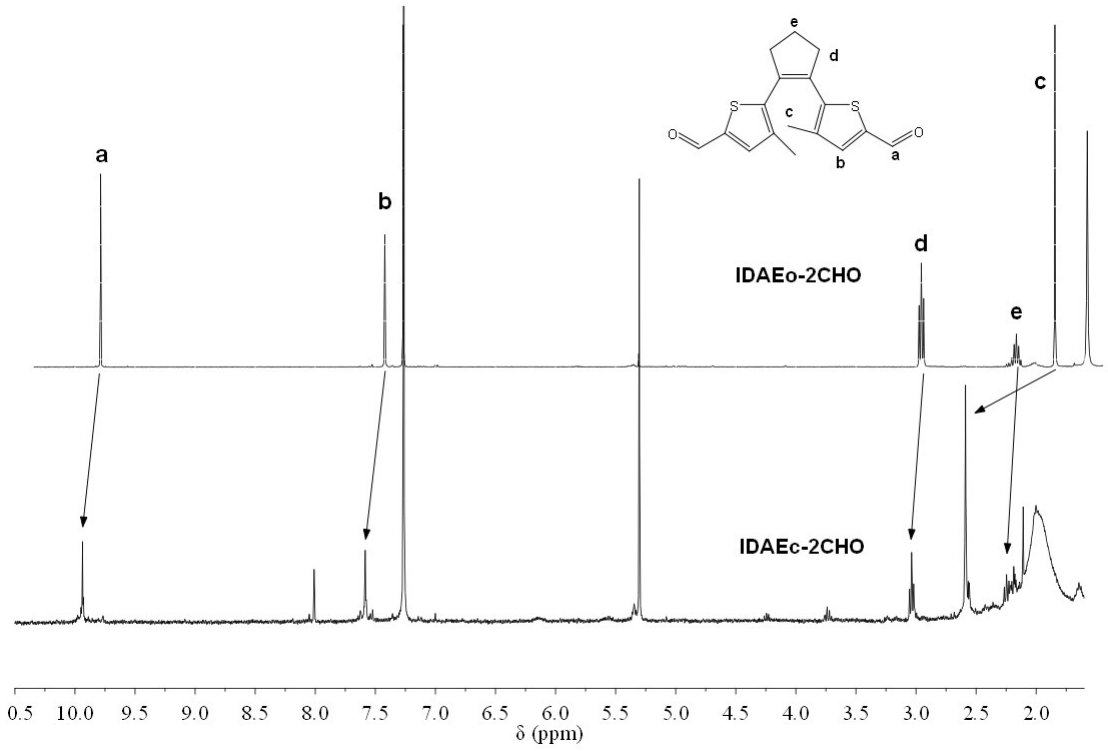


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectral changes of **IDAEo-2CHO** upon irradiation with 365 nm light.

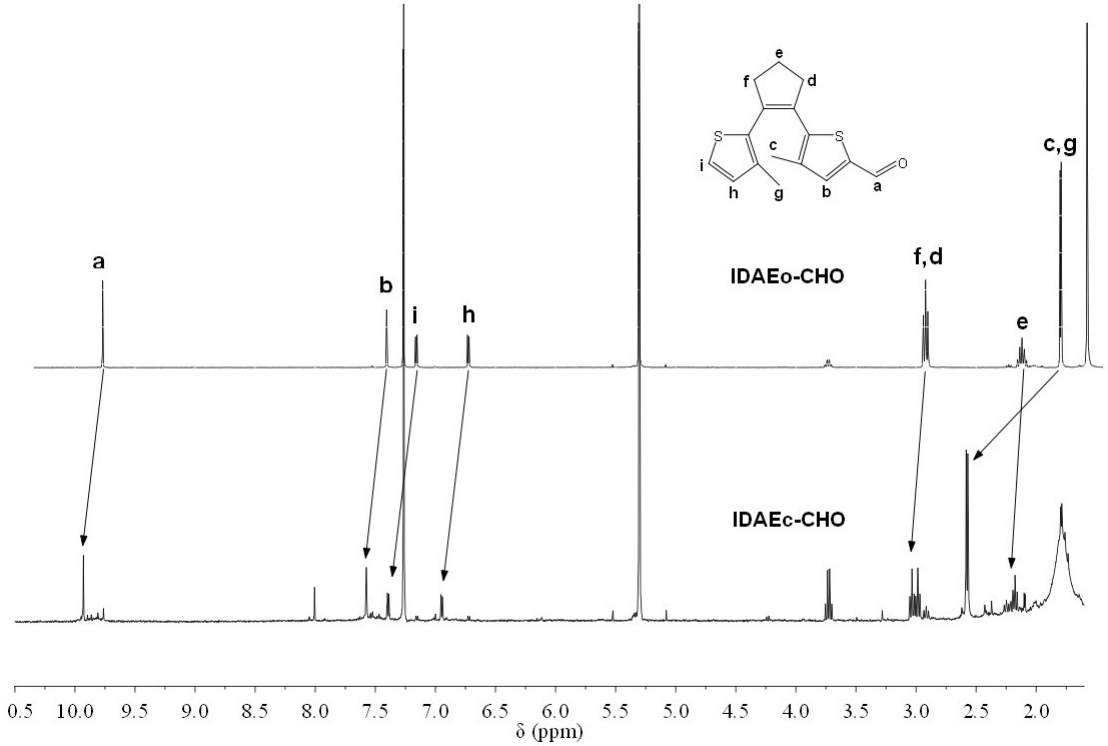


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectral changes of **IDAEo-CHO** upon irradiation with 365 nm light.

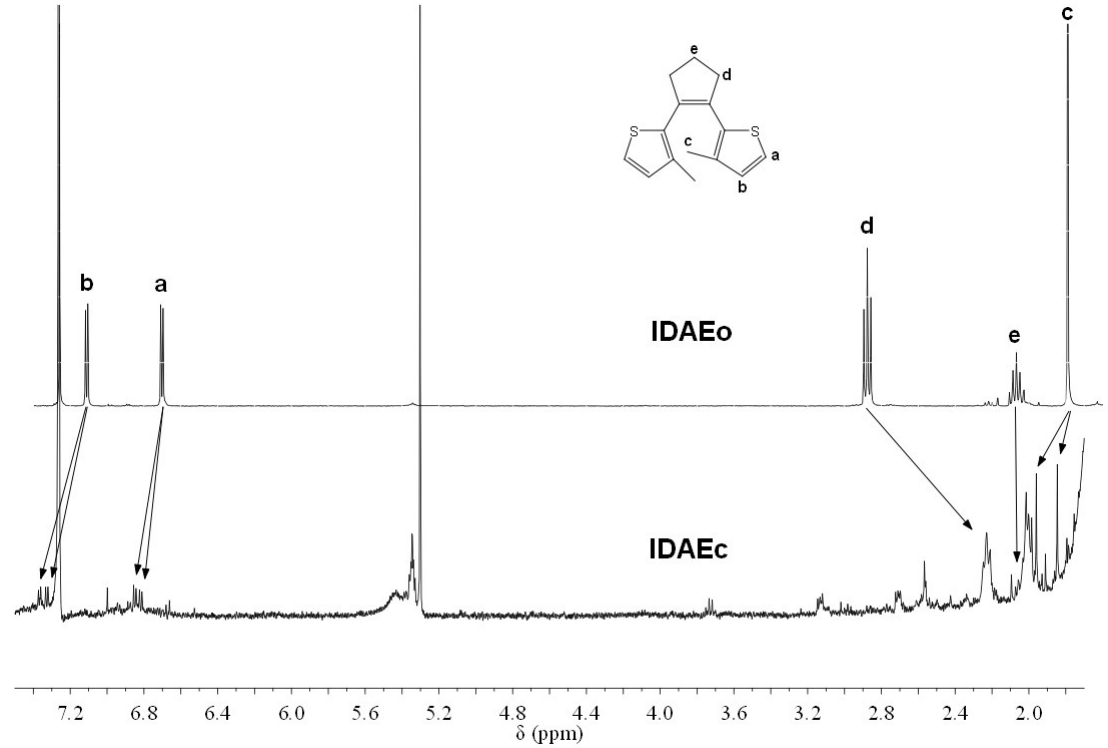


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectral changes of **IDAEo** upon irradiation with 254 nm light.

Table S1. Crystal data and structure refinement for **IDAEo-2CHO**.

Identification code	cd15003
Empirical formula	C17 H16 O2 S2
Formula weight	316.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c n
Unit cell dimensions	a = 10.9395(14) Å a= 90°. b = 8.3215(11) Å b= 90°. c = 17.160(2) Å g = 90°.
Volume	1562.1(4) $Å^3$
Z	4
Density (calculated)	1.345 Mg/m^3
Absorption coefficient	0.342 mm^{-1}
F(000)	664
Crystal size	0.211 x 0.165 x 0.123 mm^3
Theta range for data collection	2.374 to 25.993°.
Index ranges	-8<=h<=13, -10<=k<=9, -20<=l<=21
Reflections collected	8746
Independent reflections	1536 [R(int) = 0.0470]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5608
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1536 / 0 / 98
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1104
R indices (all data)	R1 = 0.0493, wR2 = 0.1185
Extinction coefficient	0.023(3)
Largest diff. peak and hole	0.235 and -0.220 $e.Å^{-3}$

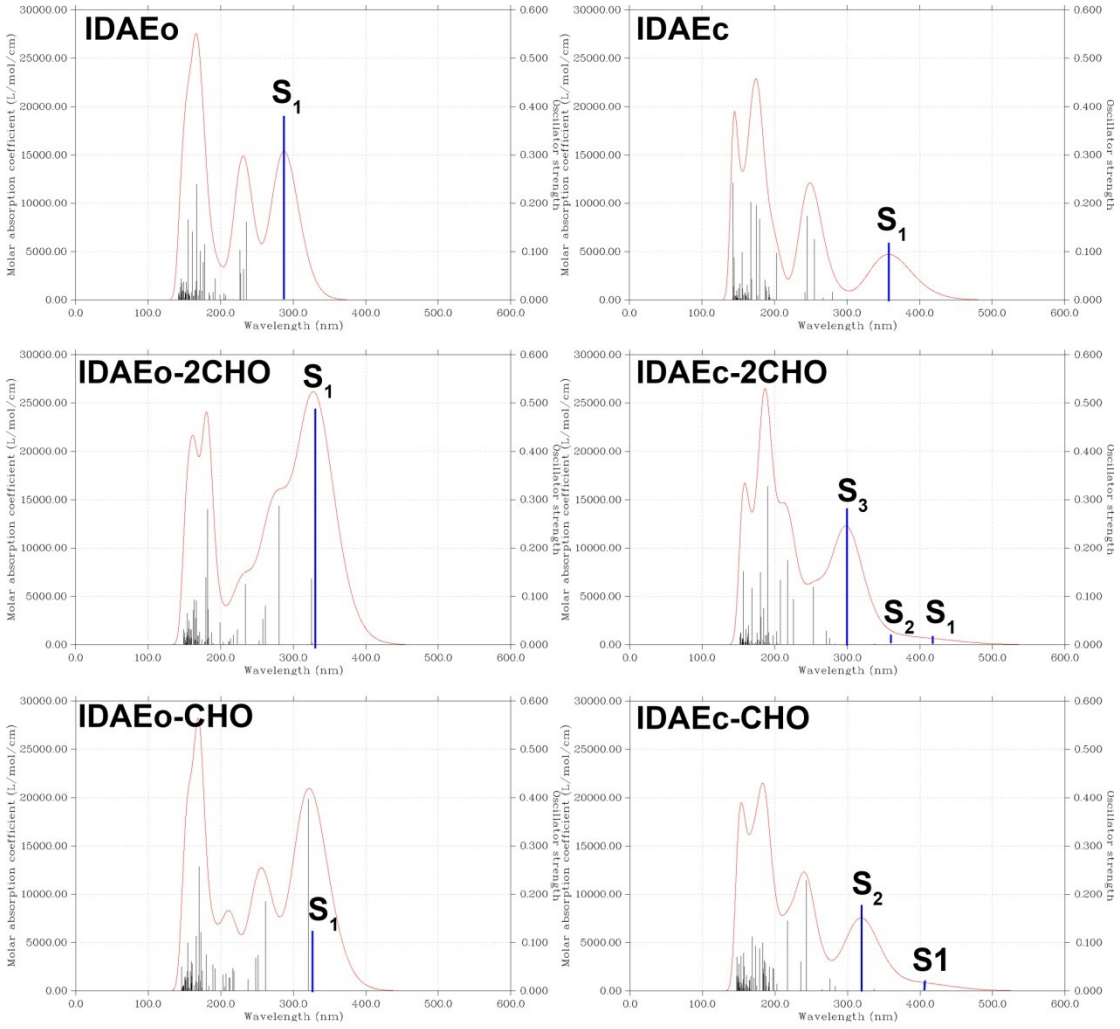


Fig. S7 The calculated absorption spectra of inverse DAEs in CH_2Cl_2 solvent. The low-energy excitation energies (wavelengths) of excited states are represented using blue lines.

Table S2. DFT calculations of lowest-energy excitation transition for **IDAE**.

compound	Excited state	Excitation energy	Oscillator strength	MO compositions
IDAEo	S_1	4.32 eV, 287.30 nm	0.3801	H→L 97.7%
IDAEc	S_1	3.47 eV, 357.24 nm	0.1167	H→L 98.1%

Table S3. DFT calculations of low-energy excitation transition for **IDAE-2CHO**.

compound	Excited state	Excitation energy	Oscillator strength	MO compositions
IDAEo-2CHO	S_1	3.75 eV, 330.72 nm	0.4886	H→L 76.8% H-6→L 5.9% H-5→L+1 5.5% H-6→L+1 2.4%
IDAEc-2CHO	S_1	2.97 eV, 417.58 nm	0.0121	H→L 92.4% H-1→L+1 3.3% H→L+2 3.1%
	S_2	3.45 eV, 359.55 nm	0.0166	H→L+1 87.7% H-1→L 6.7%
	S_3	4.13 eV, 299.95 nm	0.2827	H→L+2 91.8% H-1→L+1 2.3% H→L 2.3%

Table S4. DFT calculations of low-energy excitation transition for **IDAE-CHO**.

compound	Excited state	Excitation energy	Oscillator strength	MO compositions
IDAEo-CHO	S_1	3.81 eV, 325.58 nm	0.1229	H-5→L 52.3% H→L 25.2% H-5→L+1 8.7% H-5→L+2 3.4% H-5→L+5 2.8%
IDAEc-CHO	S_1	3.06 eV, 404.63 nm	0.0184	H→L 88.4% H→L+1 6.3% H-1→L 3.6%
	S_2	3.88 eV, 319.29 nm	0.1790	H→L+1 86.9% H-1→L 4.7% H→L 4.6%

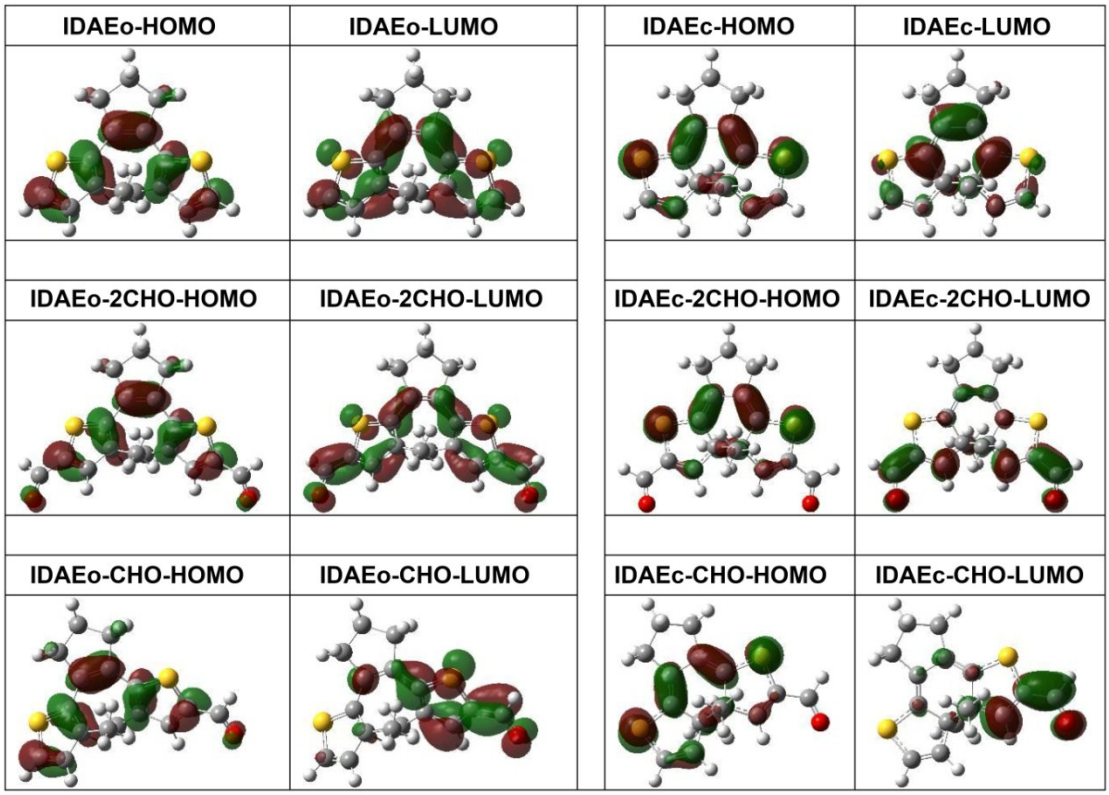


Fig. S8 Frontier molecular orbital of inverse DAEs.

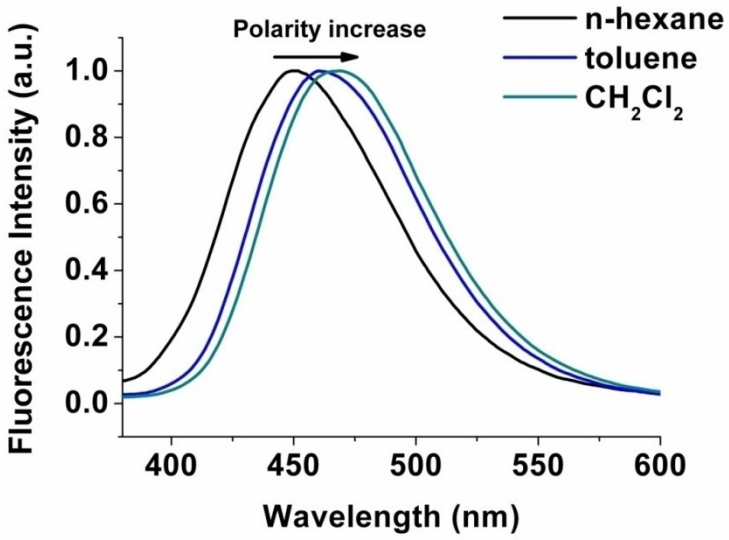


Fig. S9 Normalized fluorescence spectra of **IDAEo-2CHO** in different solvents (λ_{ex}=357nm).

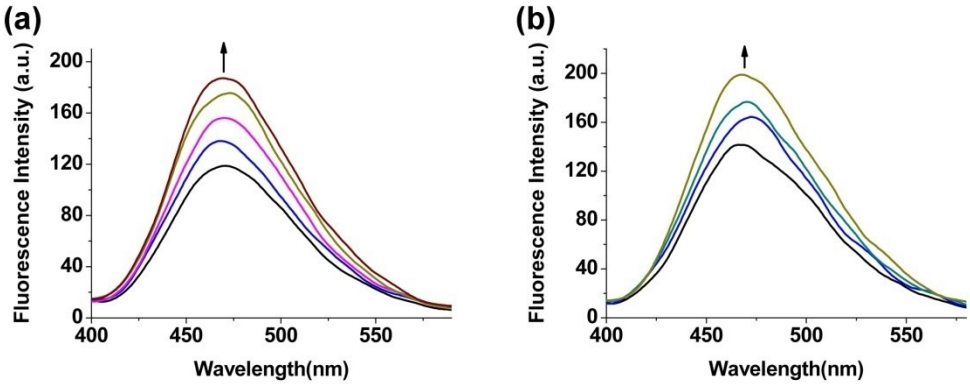


Fig. S10 (a) Fluorescence spectral changes of PSS of **IDAE-2CHO** (0.8×10^{-5} M) upon irradiation with >420 nm light in CH_2Cl_2. (b) Fluorescence spectral changes of PSS of **IDAE-2CHO** (1.0×10^{-5} M) upon irradiation with 254 nm light in CH_2Cl_2.

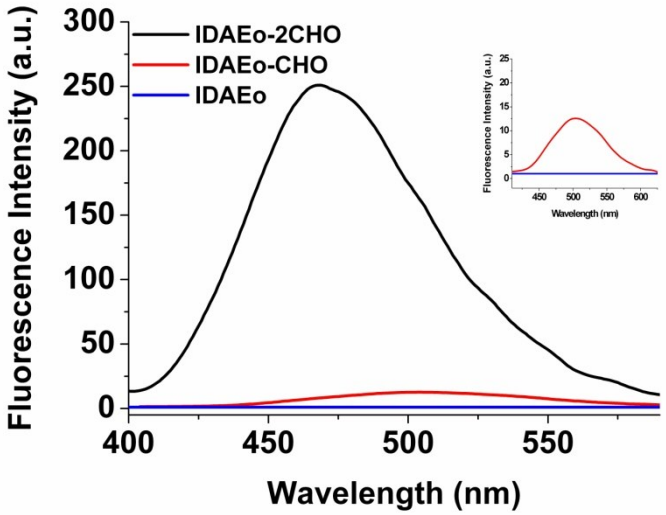


Fig. S11 The fluorescence spectra of **IDAEo** (1.0×10^{-5} M, λ_{ex} = 300 nm), **IDAEo-CHO** (1.0×10^{-5} M, λ_{ex} = 354 nm) and **IDAEo-2CHO** (1.0×10^{-5} M, λ_{ex} = 357 nm) in CH_2Cl_2. Insert: Enlarged detail of fluorescence spectra of **IDAEo** and **IDAEo-CHO**.

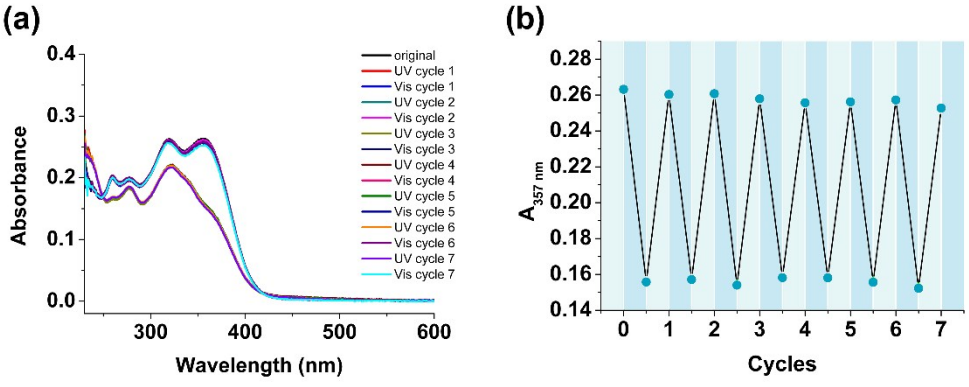


Fig. S12 (a) Absorption spectral changes in fatigue resistance measurement. (b) Absorption spectral changes of **IDAEo-2CHO** monitored at 357 nm on alternate irradiation with 365 nm light and >420 nm light in CH_2Cl_2. The data was collect from corresponding lines in (a).

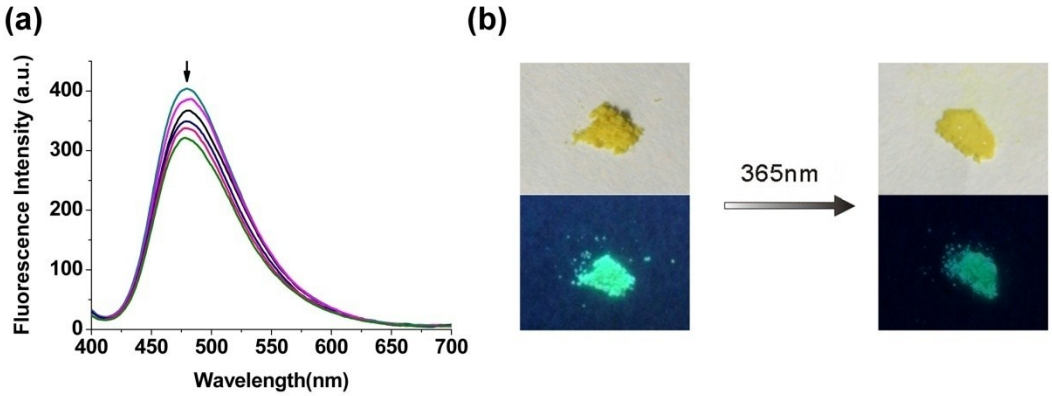


Fig. S13 (a) Fluorescence spectral changes of **IDAEo-2CHO** powders upon irradiation with 365 nm light (λ_{ex} = 365 nm). (b) Photographs of **IDAEo-2CHO** powders before and after irradiation with 365 nm light. Up: **IDAEo-2CHO** powders under room light; Down: **IDAEo-2CHO** powders under 365 nm light.

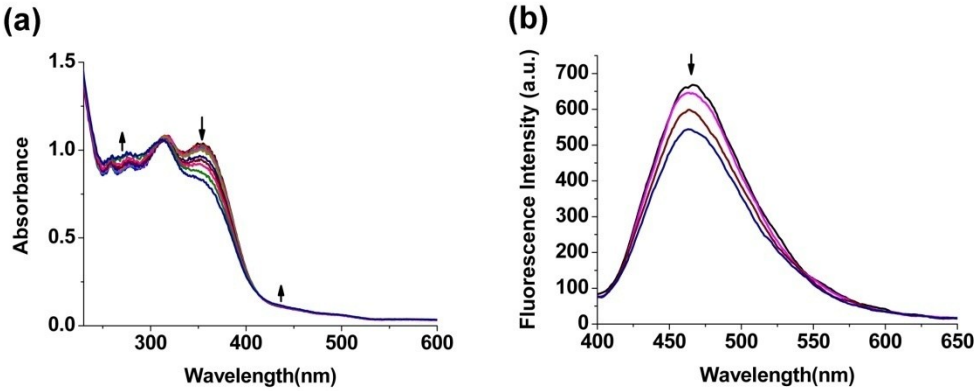


Fig. S14 Absorption (a) and fluorescence (b) spectral changes of 6 wt% **IDAEo-2CHO** - loaded PMMA film upon irradiation with 365 nm light (λ_{ex} = 353 nm).

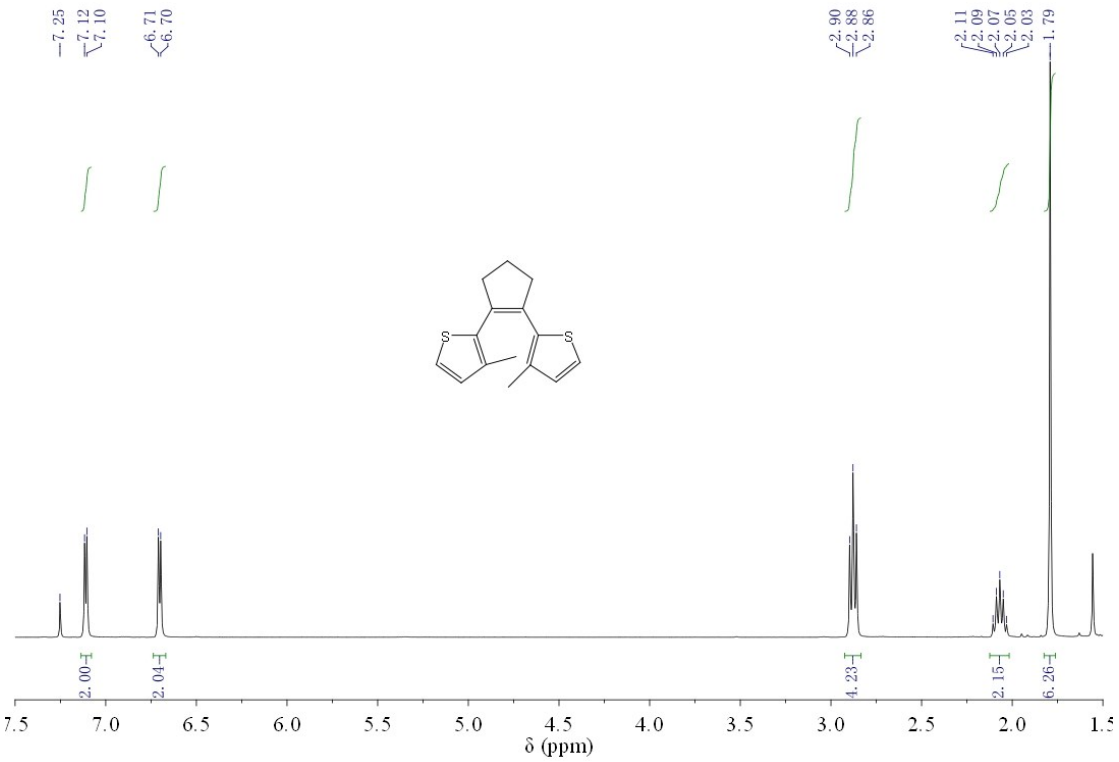


Fig. S15 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **IDAEo**.

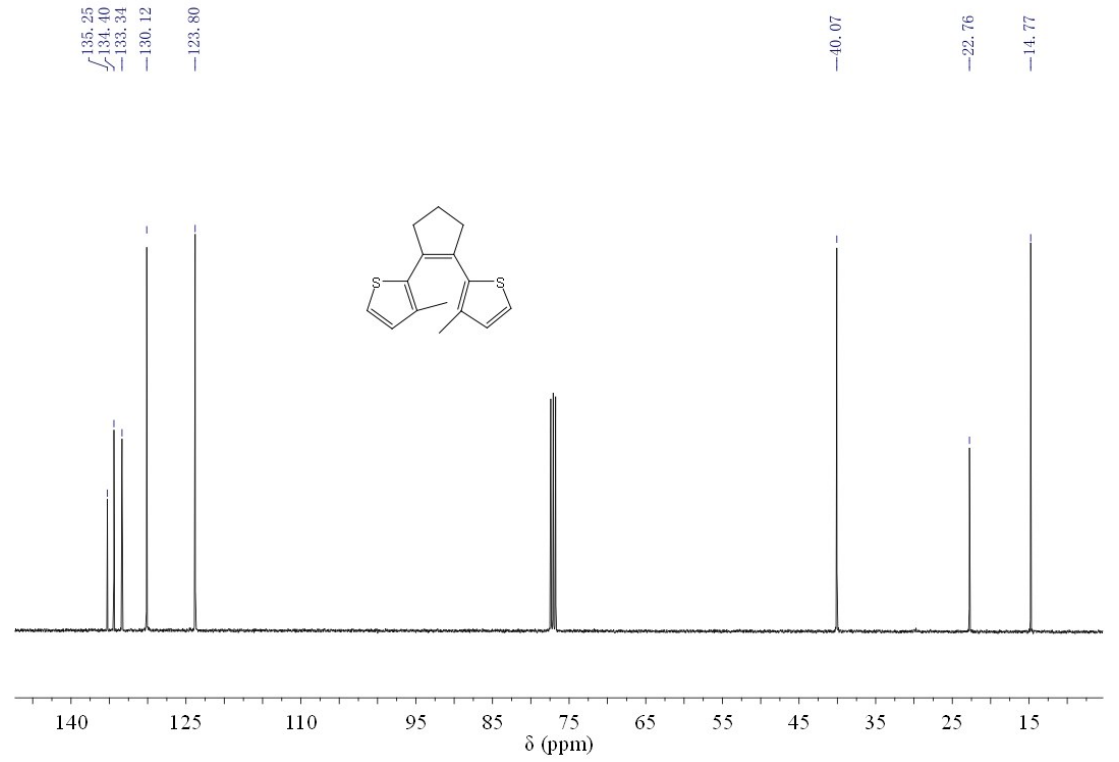


Fig. S16 ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of **IDAEo**.

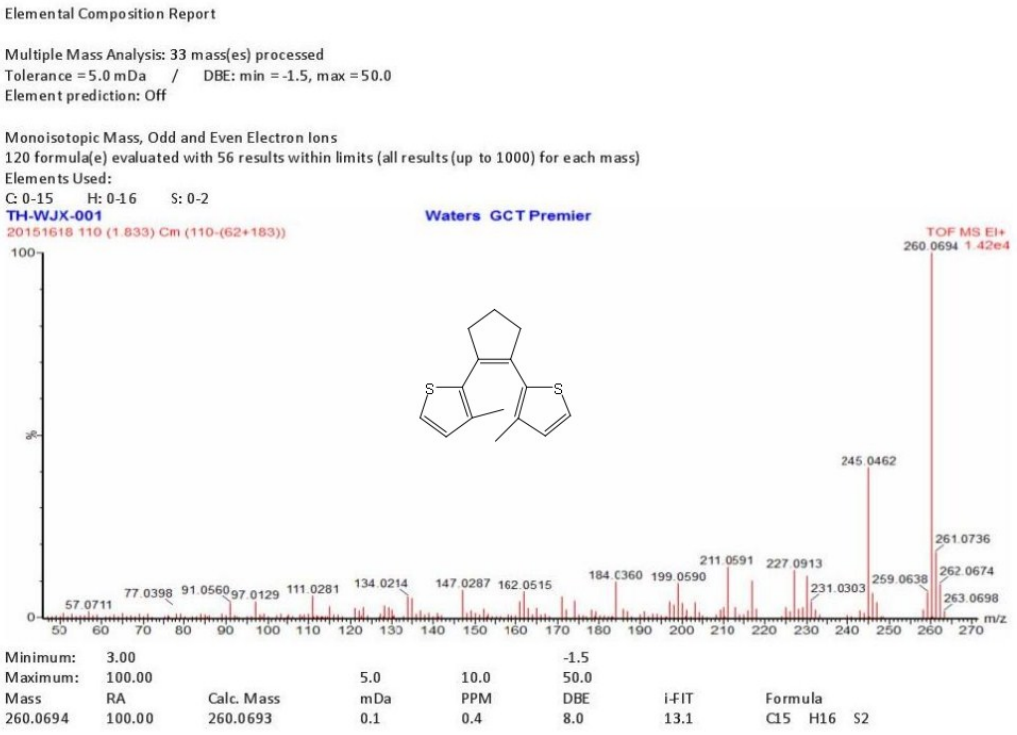


Fig. S17 HRMS (EI) spectrum of compound **IDAEo**.

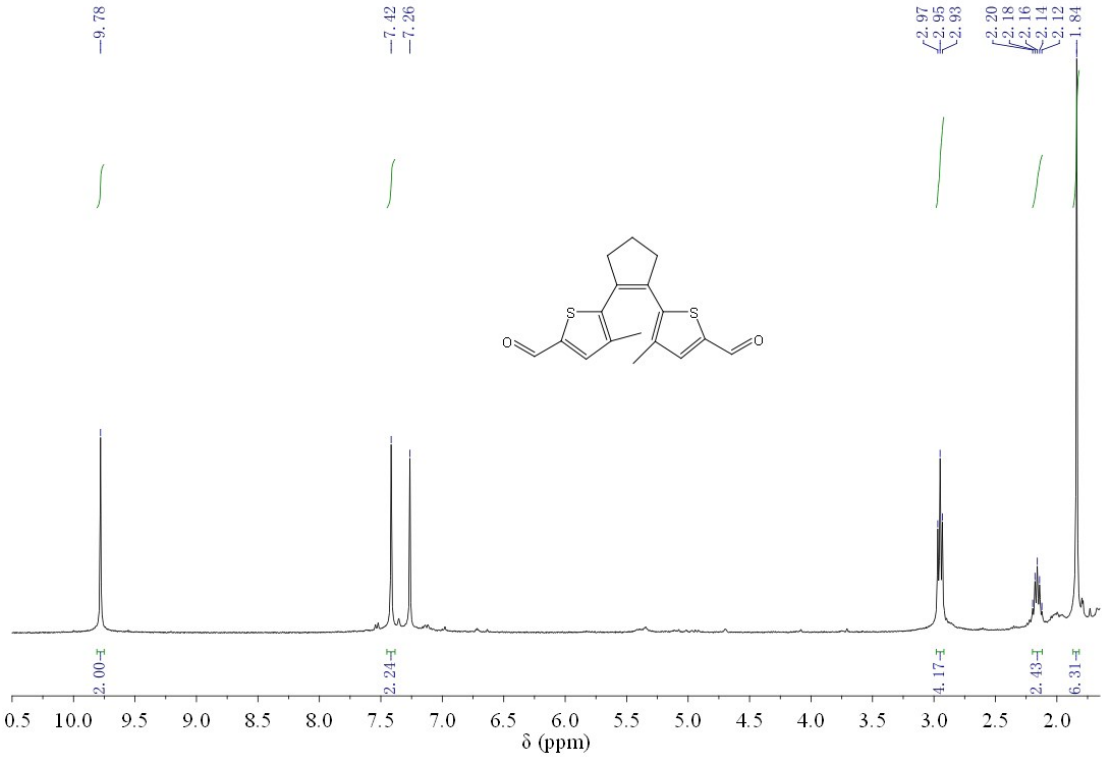


Fig. S18 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **IDAEo-2CHO**.

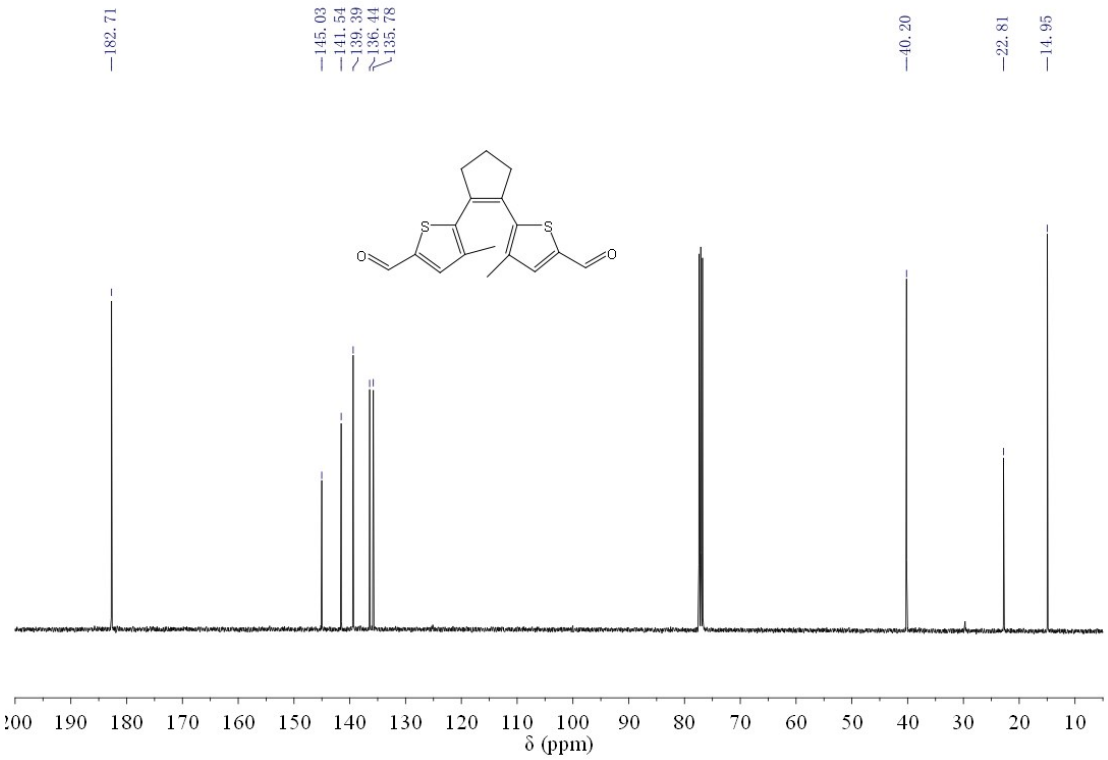


Fig. S19 ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of **IDAEo-2CHO**.

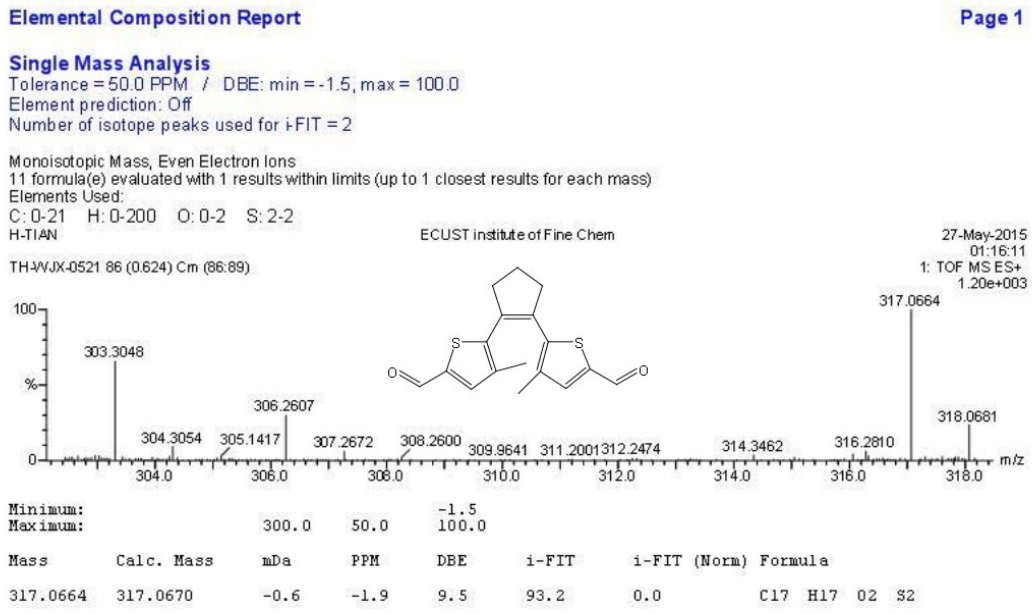


Fig. S20 HRMS (ESI) spectrum of compound **IDAEo-2CHO**.

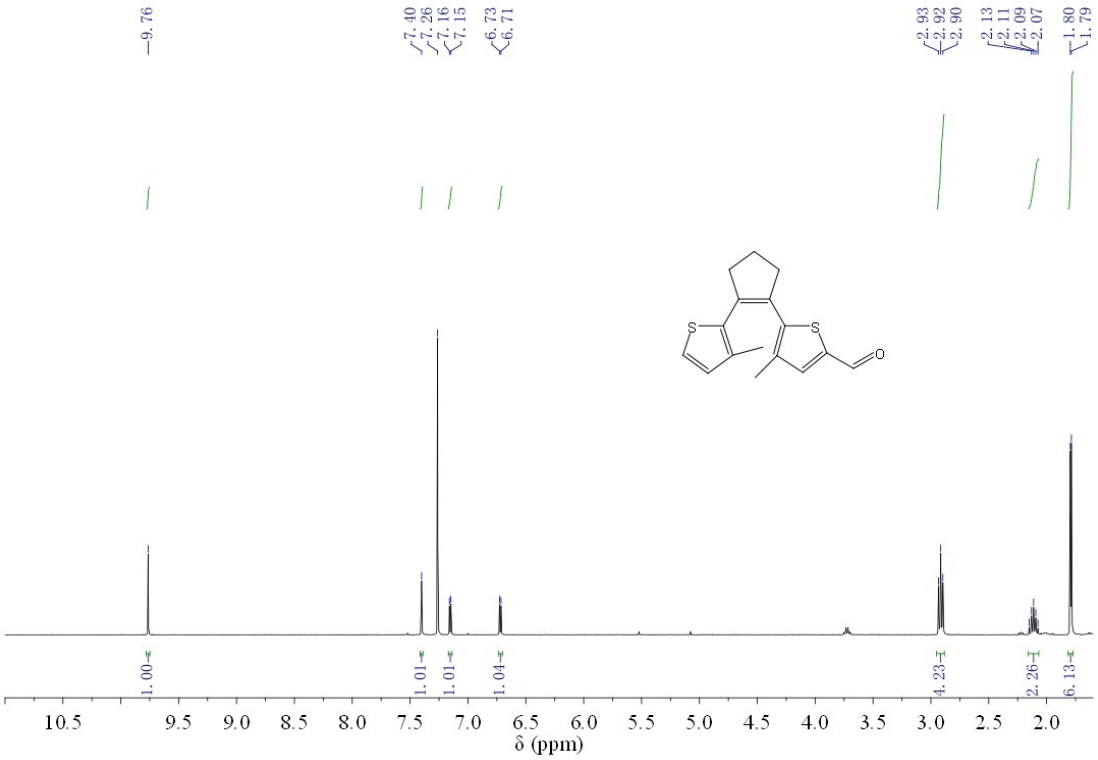


Fig. S21 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **IDAEo-CHO**.

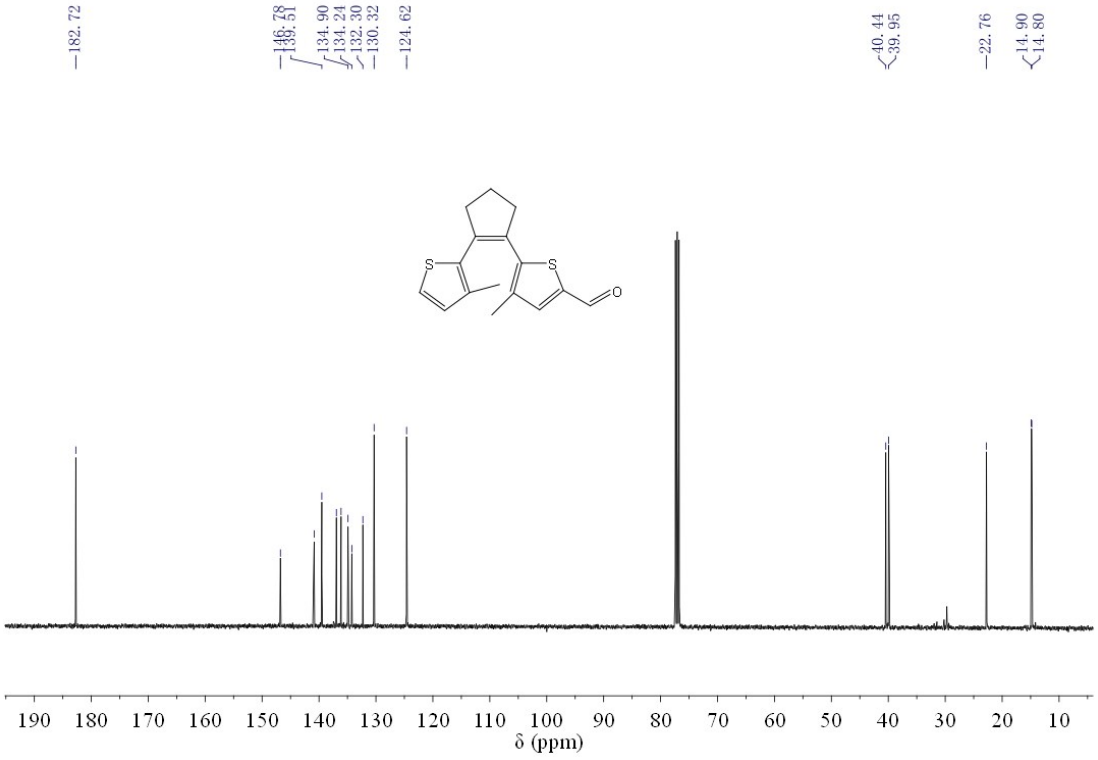
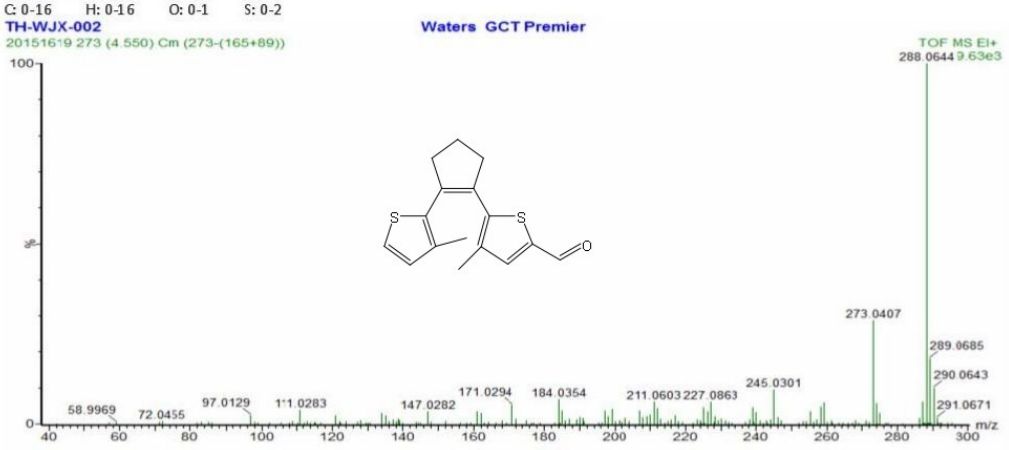


Fig. S22 ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of **IDAEo-CHO**.

Elemental Composition Report

Multiple Mass Analysis: 26 mass(es) processed
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
184 formula(e) evaluated with 41 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-16 H: 0-16 O: 0-1 S: 0-2



Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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Fig. S23 HRMS (EI) spectrum of compound **IDAEo-CHO**.