Supporting Information

for

Comprehensive Investigation of the Ultrafast Excited State Dynamics and Nonlinear Optical Properties of Pyrene Derivatives with Different Push-Pull Properties

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Key words: Pyrene derivatives, transient absorption spectroscopy, non-linear optics

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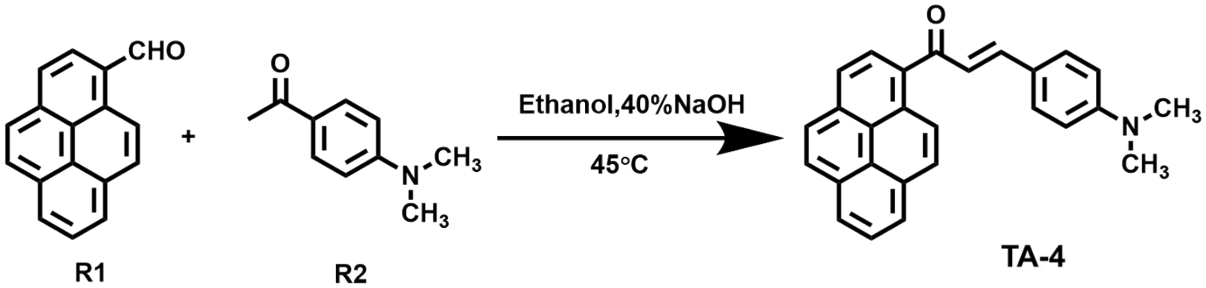
Table of Contents

Section **Page Number**

S1. Material and Methods

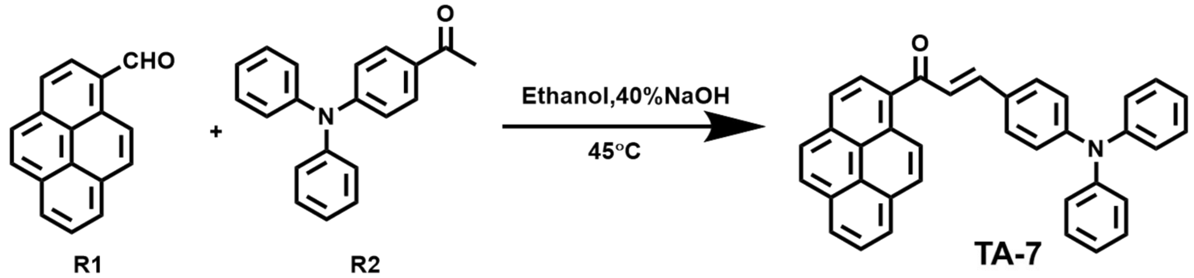
Synthesis of pyrene derivatives (TA-4, TA-7, TA-8)



Synthetic procedures of TA-4:

Scheme S1. The synthetic method was employed to prepare **TA-4.**

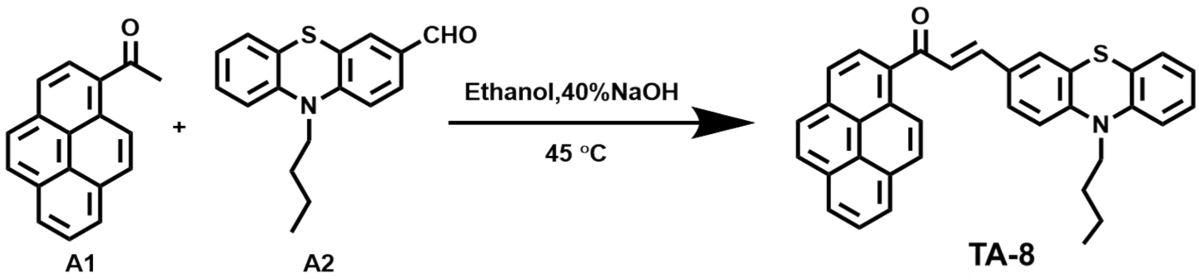
The pyrene derivatives were synthesized by Claisen-Schmidt condensation reaction using aldehyde with respective ketones. 1-(4-(dimethylamino)phenyl)ethan-1-one (0.009 mol) and 1-pyrenealdehyde (0.009 mol) were dissolved in absolute ethanol and stirred for about 10 min to get homogeneous solution at room temperature. The sodium hydroxide (0.018 mol) was dissolved in a minimum amount of water and added drop wise to the homogenous mixture with time interval of 20 min. A light brown colour reaction mixture turns to yellow colour precipitate, which was then stirred for 6 h at 10 °C. The completion of reaction was monitored by TLC technique. At the end of the reaction, resultant mixture was quenched with ice water, and set-a-side for 4 h to form a yellow colour precipitate which was filtered, dried for 12 h and purified by column chromatography to get the product. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.54 (d, J = 9.2 Hz, 1H), 8.20 (s, 5H), 8.17 – 8.07 (m, 4H), 8.03 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 0.7 Hz, 1H), 6.65 (d, J = 9.0 Hz, 2H), 3.02 (s, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 196.77, 152.24, 147.72, 135.24, 132.78, 131.29, 130.88, 130.62, 129.16, 128.84, 128.74, 127.37, 126.36, 126.04, 125.91, 125.81, 125.11, 124.98, 124.64, 124.23, 122.86, 122.36, 111.90, 40.21.



Synthetic Procedure of TA-7:

Scheme S2. The synthetic method was employed to prepare **TA-7.**

2.04 mmol of R1 and 2.04 mmol of R2 were taken in round bottom flask and 30 mL ethanol was added in the mixture was stirred at 45 °C for 10-15 minutes to get homogeneous solution. In another beaker 1.6g NaOH was dissolved in 4mL water which base solution was added dropwise by glass rod to mixture solution in interval of 15-20 minutes and solution became yellow color. Then the reaction mixture was further stirred at 40 °C for overnight. The progress of the reaction was monitored by TLC. After 6 h, the starting materials R1 and R2 disappeared indicating the completion of the reaction. The reaction was quenched by the addition of ice-water. The orange-colored precipitate was formed, and the precipitate was filtered in 90% yield. ^{1}**H** NMR (500 MHz, CHLOROFORM-*D*) δ 8.97 (d, J = 15.4 Hz, 1H), 8.58 (d, J = 9.3 Hz, 1H), 8.40 (d, J = 8.1 Hz, 1H), 8.24 – 8.16 (m, 4H), 8.12 (d, J = 8.9 Hz, 1H), 8.07 (s, 1H), 8.06 – 8.00 (m, 3H), 7.81 (d, J = 15.3 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.22 – 7.12 (m, 6H), 7.10 – 7.05 (m, 2H). ^{13}**C NMR** (126 MHz, CHLOROFORM-D) δ 188.03, 152.26, 146.58, 140.37, 132.82, 131.43, 130.84, 130.35, 129.75, 129.32, 128.69, 127.45, 126.40, 126.13, 125.94, 125.14, 124.80, 124.31, 124.12, 122.90, 119.98.



Synthesis Procedure of TA-8:

Scheme S3. The synthetic method was employed to prepare **TA-8.**

0.55g A1(2.26mmol) and 0.64g(2.26mmol) A2 were taken in round bottom flask and 30 mL ethanol was added in the mixture was stirred at 45 °C for 10-15 minutes to get homogeneous solution. In another beaker 1.6g NaOH was dissolved in 4mL water which solution was dropwise added to the mixture of solution in interval of 15-20 minutes and solution became orange color. Then the reaction mixture was further stirred at 45°C for overnight. The progress of the reaction was monitored by TLC. After 6h, the starting materials A1 and A2 disappeared indicating the completion of the reaction. The reaction was quenched by the addition of ice-water. The red colored precipitate was formed, and the precipitate was filtered and obtained in 95% yield. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.58 (d, J = 9.3 Hz, 1H), 8.29 – 8.21 (m, 4H), 8.17 (dd, J = 9.1, 4.8 Hz, 2H), 8.12 (d, J = 8.9 Hz, 1H), 8.06 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 15.9 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.19 – 7.06 (m, 2H), 6.93 (td, J = 7.5, 1.1 Hz, 1H), 6.89 – 6.80 (m, 2H), 3.89 – 3.83 (m, 2H), 1.83 – 1.74 (m, 2H), 1.51 – 1.41 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 196.05, 147.63, 145.23, 144.15, 134.35, 133.19, 131.26, 130.80, 129.36, 129.08, 128.97, 128.77, 127.60, 127.54, 127.34, 126.97, 126.47, 126.23, 126.14, 126.00, 125.40, 125.22, 124.99, 124.90, 124.56, 124.22, 123.90, 123.12, 115.72, 115.31, 47.50, 28.94, 20.21, 13.90.

S2. Steady-state and time resolved spectroscopy

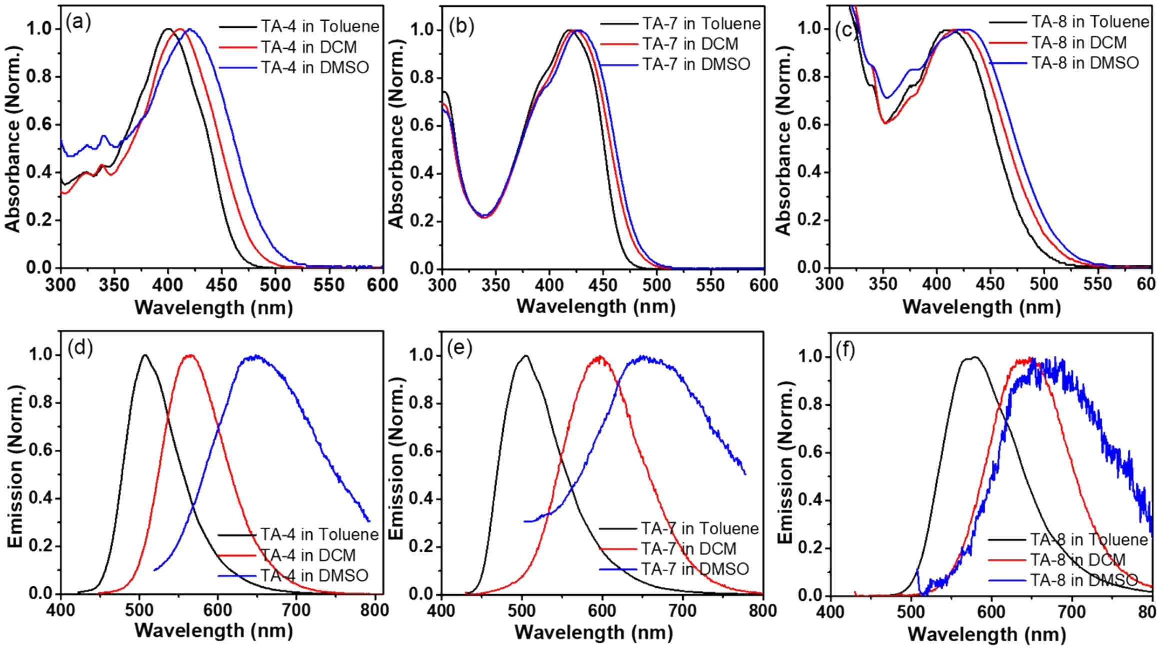


Figure S1: (a-c) Steady-state absorption and (d-f) emission spectra of (a,d) **TA-4**, (b,e) **TA-7**, and (c,f) **TA-8** in toluene, DCM, and DMSO.

Table S1:

	λ_{abs}^{max} (nm)			λ_{em}^{max} (nm)		
	Toluene	**DCM**	**DMSO**	**Toluene**	**DCM**	**DMSO**
TA-4	400	411	419	507	564	643
TA-7	418	423	427	506	597	652
TA-8	411	420	427	567, 580	640	667

Photophysical properties of **TA-4**, **TA-7**, and **TA-8** compounds.

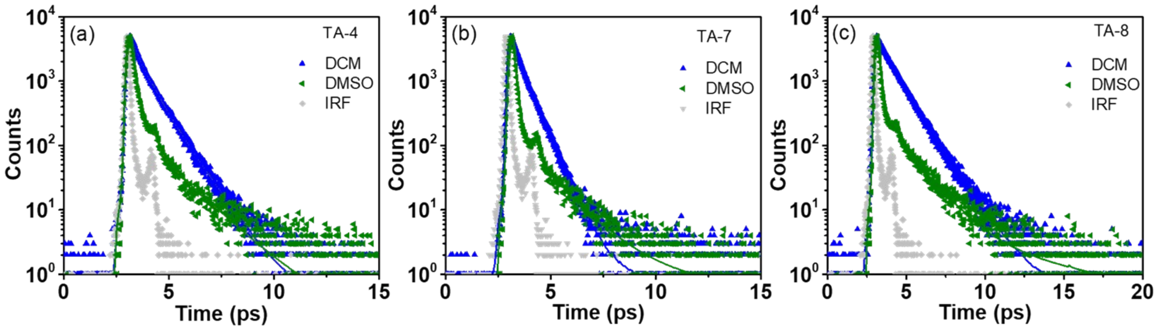


Figure S2: TCSPC curves of (a) **TA-4**, (b) **TA-7**, and (c) **TA-8** in DCM and DMSO.

Table S2: Fluorescence Lifetimes of pyrene derivatives in DCM and DMSO.

Compound	**Solvent**	$\tau_1(\alpha_1)$, **ns**	$\tau_2(\alpha_2)$, **ns**	τ_{avg}, **ns**	**χ²**	$k_r \times$ **(10⁸)** s^{-1}	$k_{nr} \times$ **(10⁸)** s^{-1}
TA-4	DCM	0.35 (0.46)	0.90 (0.53)	0.76 ± 0.01	0.99	0.13	13.0
	DMSO	0.16 (0.87)	1.46 (0.12)	0.90 ± 0.02	1.04	-	-
TA-7	DCM	0.33 (0.56)	0.62 (0.43)	0.50 ± 0.01	1.02	0.70	19.30
	DMSO	0.10 (0.90)	1.50 (0.09)	0.96 ± 0.02	1.02	-	-
TA-8	DCM	0.74 (0.54)	1.27 (0.45)	1.05 ± 0.02	1.10	0.17	9.35

	DMSO	0.11 (0.78)	1.66 (0.21)	1.35 ± 0.03	1.05	-	-

τ_{avg}= Average Lifetime

The radiative and nonradiative rate constant values are calculated using the following equations S2 and S3.

$$k_r = {}^{\Phi_F}/_{\tau} \qquad \text{(S1)}$$

$$k_{nr} = {}^{(1 - \Phi_F)}/_{\tau} \qquad \text{(S2)}$$

Where, Φ_F is the fluorescence quantum yield, and τ is the fluorescence lifetime of the compound.

Table S3: Fluorescence quantum yields of **TA-4**, **TA-7** and **TA-8** obtained using relative method.

Compound	**Absorbance**			**Integrated fluorescence intensity**			**Quantum yield**	
	1	2	3	1	2	3	Φ_i	Φ_{avg}
TA-4	0.12	0.09	0.05	29566880	19386560	14461490	0.012 0.009 0.008	0.010
TA-7	0.11	0.07	0.04	86475960	62897595	40347165	0.039 0.037 0.030	0.035
TA-8	0.13	0.07	0.06	57730315	32728990	28726810	0.022 0.019 0.014	0.018
Anthracene	0.07	0.04	0.02	165933095	103666225	67453445	0.36	-
BPA	0.03	0.02	0.01	604650860	473085965	328852375	1	-

The fluorescence quantum yield, Φ of the compounds was calculated using the relative method by taking anthracene and BPA as a reference dye and using the following equation S1.

$$\Phi = \Phi_R({}^{I}/_{I_R})({}^{A_R}/_{A})({}^{\lambda_{exR}}/_{\lambda_{ex}})({}^{n^2}/_{n_R^2}) \qquad \text{(S3)}$$

where $\varnothing_R$ is the quantum yield of reference dye, I and I_R are integrated fluorescence intensities of compounds and reference dye, respectively, A and A_R are the absorbance of the compounds and reference dye, respectively, and n and n_R are the refractive indices of solvent(s) used for compounds and reference, respectively.

S3. Transient Absorption Spectroscopy

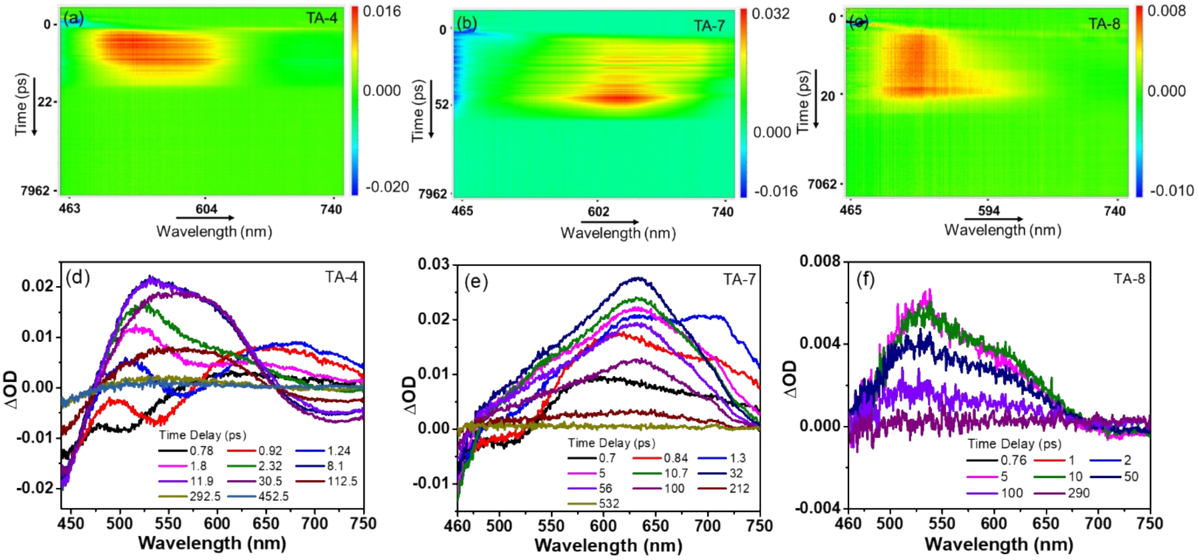


Figure S3: (a-c) 2D pseudocolor plot and (d-f) transient absorption spectra (ΔOD vs wavelength, nm) at selected time delay of (a,d) **TA-4**, (b,e) **TA-7**, and (c,f) **TA-8** in DMSO taken after photo excitation with a 420 nm laser source probed within 420-750 nm range at different time delays ranging from hundreds of fs to 8 ns.

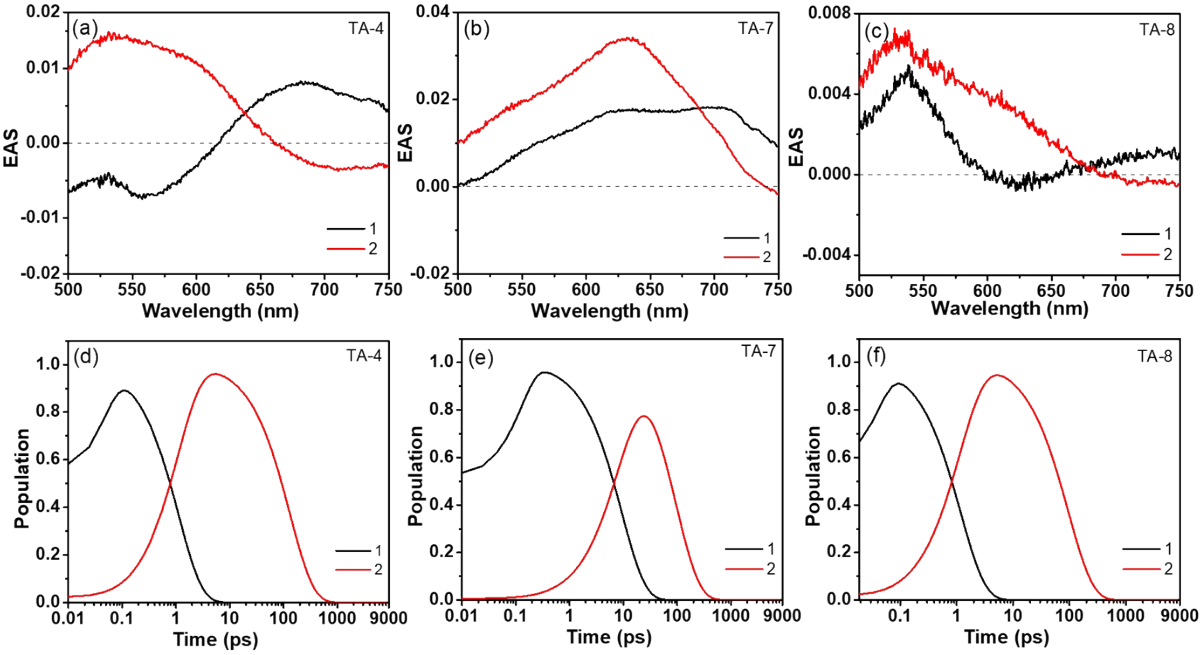
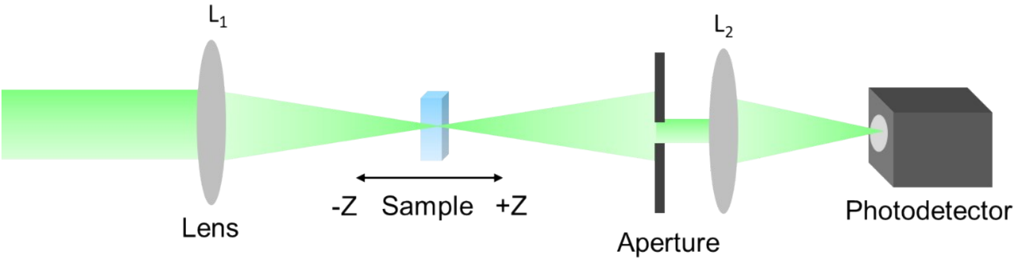


Figure S4: (a-c) Evolution-associated spectra (EAS) and (d-f) respective population dynamics of **TA-4, TA-7,** and **TA-8** in DMSO.



S4. Z-scan technique

Figure S5: Schematic representation of Z-scan set-up.

In the Z-scan experiments, a 750 nm beam with a pulse width of 100 fs and a repetition rate of 1 kHz is used to investigate the nonlinear optical (NLO) properties of the sample. We are using a Libra Ultrafast Amplifier Laser System, which has a high-quality factor of ~ 1.1. The input laser beam is focused using a convex lens L_1, and the sample placed inside a quartz cuvette is translated around the focus from –Z to +Z axis by a motorized stage. The transmitted beam is detected by a photodetector. The sample's nonlinear absorption (NLA) and nonlinear refraction

(NLR) were characterized using open aperture (OA) and closed aperture (CA) configurations. In the CA configuration, the NLR is determined by collecting the transmitted beam through a slit, while in the OA configuration, the NLA values were obtained by collecting the transmitted beam directly without the use of a slit.

The Z-scan data were numerically fitted by Sheik Bahae's theory to obtain the two-photon absorption (2PA) coefficient (β) value.[1]

The normalized OA *Z*-scan data is fitted with the following transmittance equation

$$T(z) = 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}(1 + x^2)} \quad \text{(S4)}$$

Where, $x = {}^{z}/_{z_R}$, z_R is the Rayleigh range, z is the translation direction coordinate, β is the nonlinear absorption coefficient, and L_{eff} is the effective sample length.

The CA Z-scan traces are fitted using the following equation

$$T(z) = 1 - \frac{4x\Delta\Phi}{(1 + x^2)(9 + x^2)} + \frac{2(3 + x^2)\Delta\varphi}{(1 + x^2)(9 + x^2)} \quad \text{(S5)}$$

ΔΦ is the nonlinear phase shift and $\Delta\varphi$ is the phase shift due to NLA.

$$\Delta\Phi = \frac{2\pi}{\lambda} n_2 I_0 L_{eff} \quad \text{(S6)}$$

Where, n_2 is the nonlinear refractive indices.

S5. ^{1}H NMR, and ^{13}C NMR of the compounds

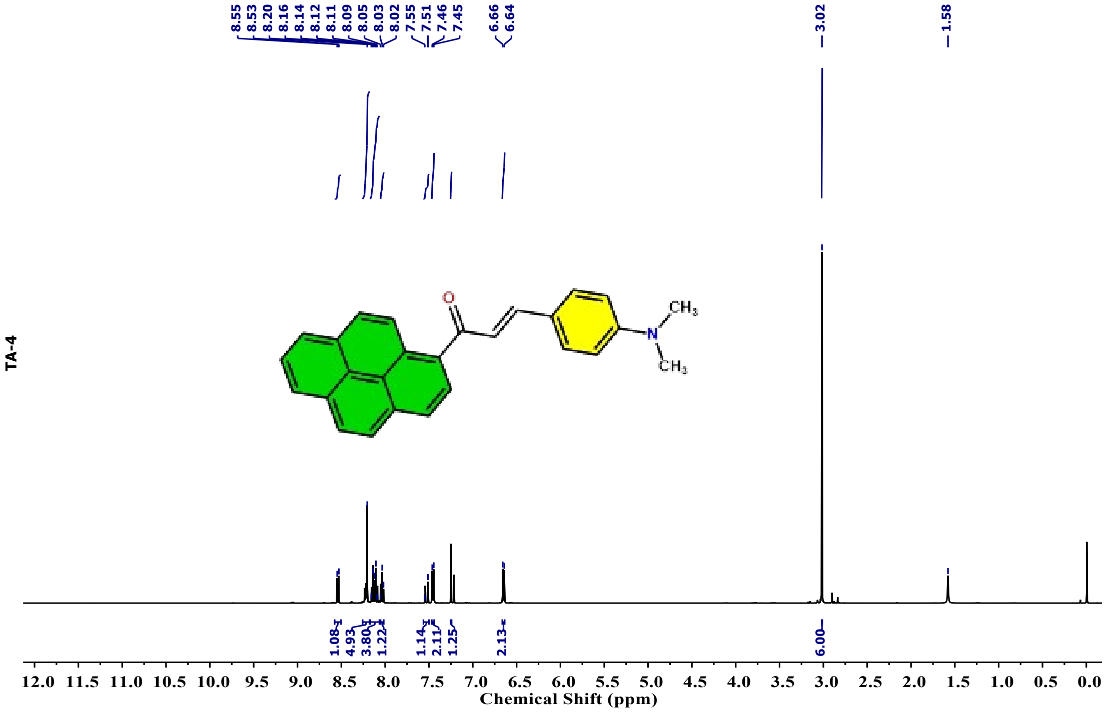


Figure S6: ^{1}H NMR spectrum of **TA-4** in CDCl3.

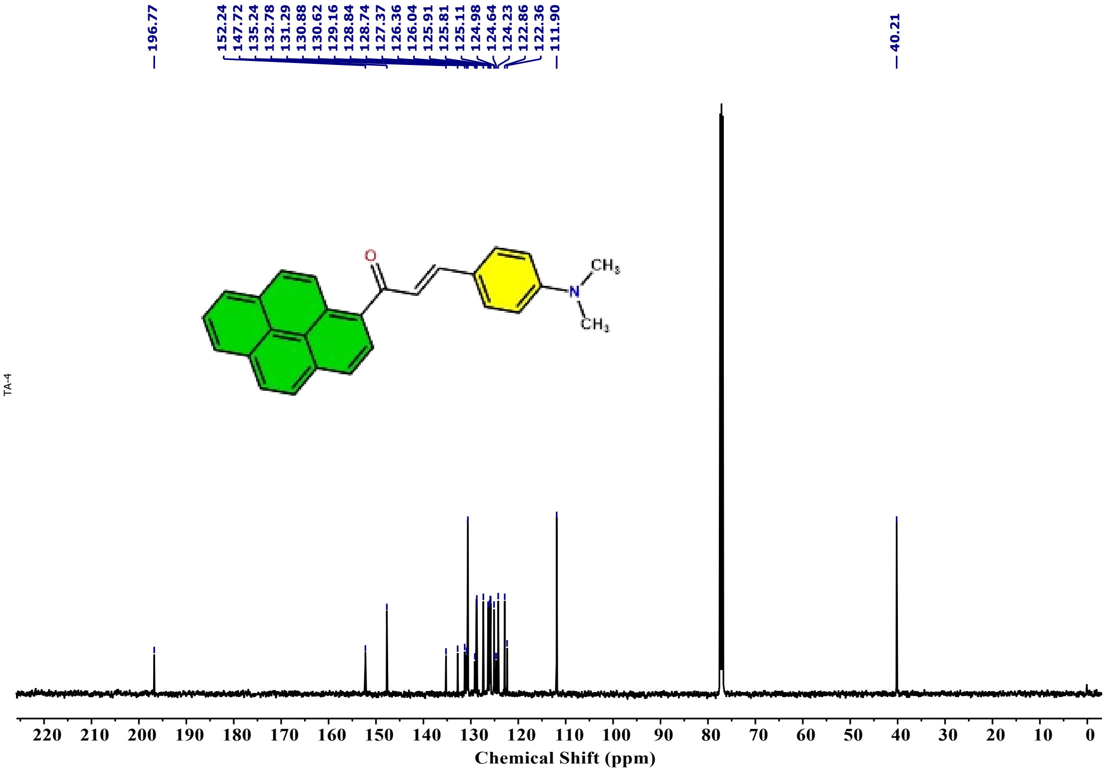


Figure S7: ^{13}C NMR spectrum of **TA-4** in CDCl3.

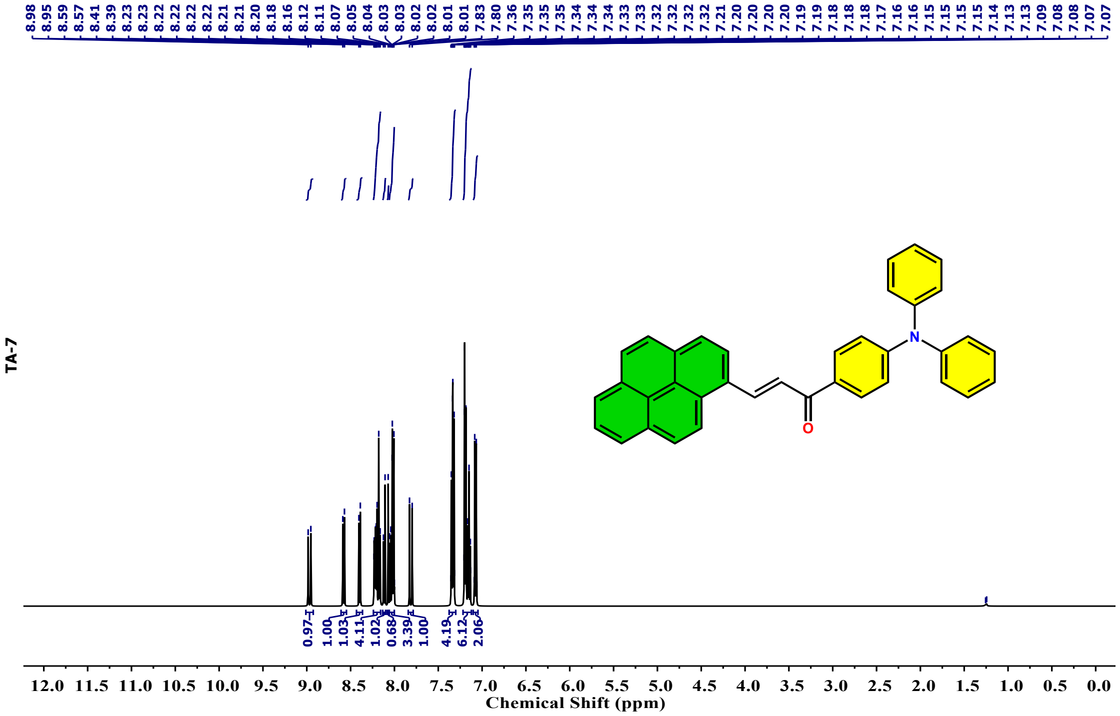


Figure S8: ^{1}H NMR spectrum of **TA-7** in CDCl3.

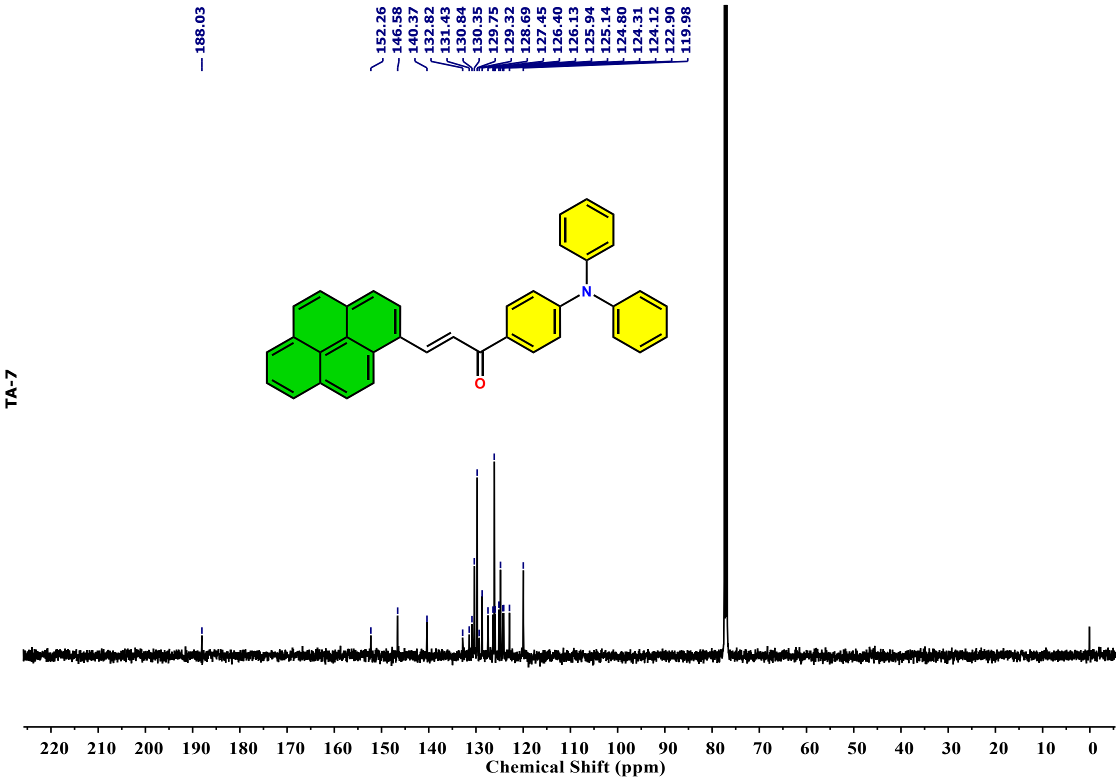


Figure S9: ^{13}C NMR spectrum of **TA-7** in CDCl3.

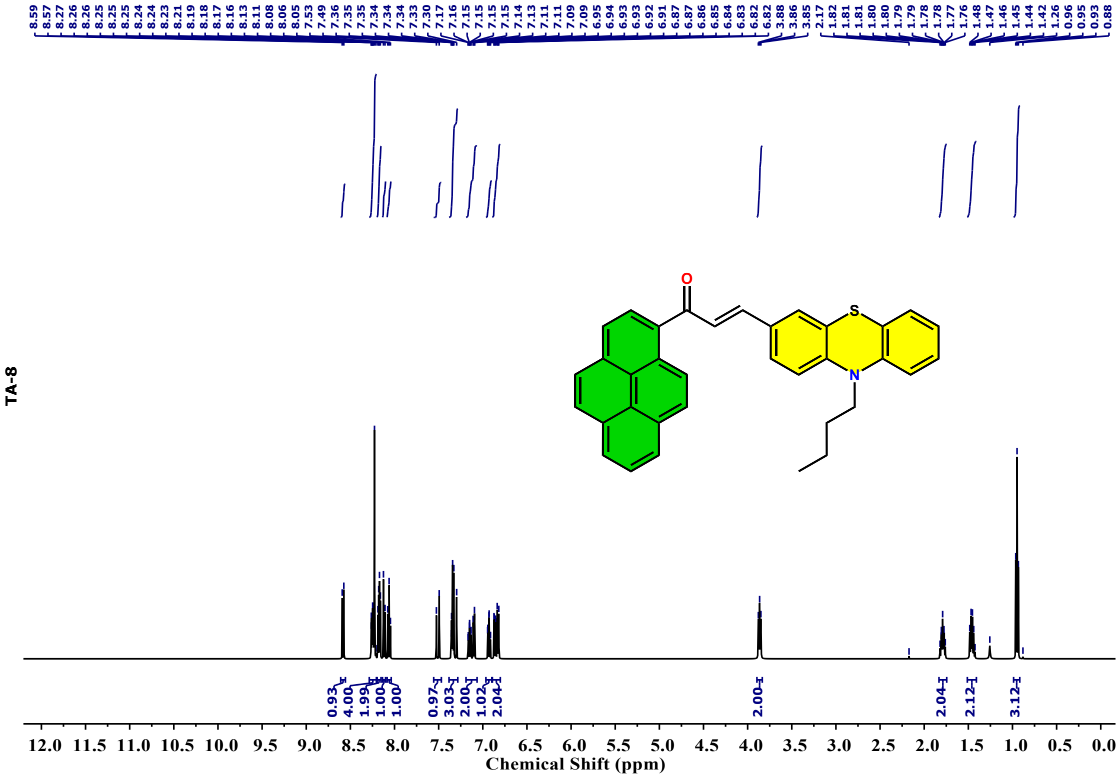


Figure S10: ^{1}H NMR spectrum of **TA-8** in CDCl3.

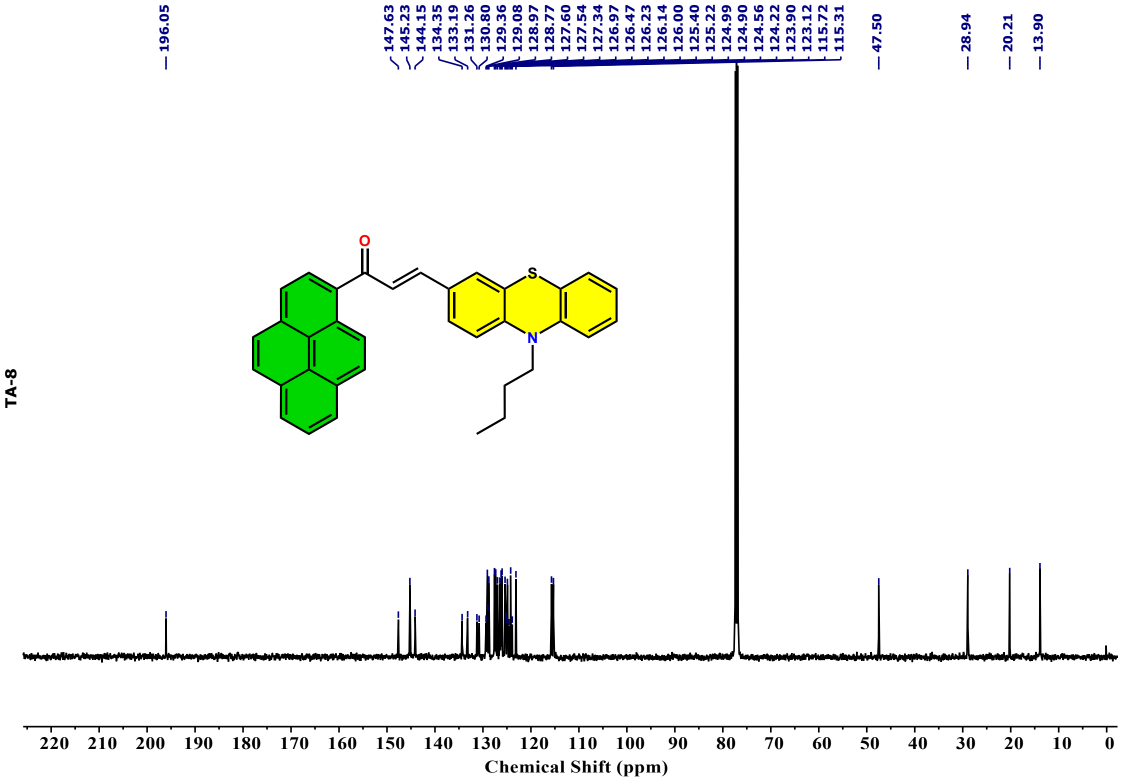


Figure S11: ^{13}C NMR spectrum of **TA-8** in CDCl3.

S6. References

(1) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. Sensitive Measurement of Optical Nonlinearities Using a Single Beam. *IEEE J. Quantum Electron.* **1990**, *26* (4), 760–769. .