

Supporting Information

Multibranched triarylamine end-capped oxime esters as visible-light absorbing Type I photoinitiators for free radical photopolymerization

**Yu-Hao Wu^a, Adel Noon^{b,c,d}, Fatima Hammoud^{b,c}, Tayssir Hamieh^d, Joumana Toufaily^d,
Bernadette Graff^{b,c}, Jacques Lalevée^{b,c*}, Yung-Chung Chen^{a,e*}**

^a. Department of Chemical and Materials Engineering, National Kaohsiung University of Science and Technology, Kaohsiung 807618, Taiwan

^b. Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100, Mulhouse, France

^c. Université de Strasbourg, Strasbourg, France

^d. Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), Faculty of Sciences, Doctoral School of Sciences and Technology (EDST), Lebanese University, Beirut 6573-14, Lebanon

^e. Photo-SMART (Photo-sensitive Material Advanced Research and Technology Center), National Kaohsiung University of Science and Technology, Kaohsiung City 807618, Taiwan

*Corresponding authors: Jacques Lalevée (jacques.lalevee@uha.fr)

Yung-Chung Chen (chenyc@nkust.edu.tw)

1. Synthesis of TP-1M

To a round-bottomed flask was added **TP-1-OH**¹ (1.5 g, 5.21 mmol), TEA (1.45 mL, 10.41 mmol), acetic anhydride (0.54 mL, 5.73 mmol) and dissolved in CHCl₃ (20 mL). The reaction mixture was stirred and heated at 60 °C for 4 h. After complete the reaction, the solution was extracted with DCM and H₂O. The organic phase was collected and dried over MgSO₄. Finally, the crude product was purified through silica chromatography using n-Hexane/EA (2/1 by vol.) as eluent. The white solid of **TP-1M** was obtained (1.55 g, 90%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.255 (s, 1H, C=N-H), 7.555 – 7.533 (dd, 2H, J = 8.8, 2.8 Hz, Ar-H), 7.325 – 7.275 (4H, Ar-H), 7.168 – 7.087 (6H, Ar-H), 7.022 – 6.993 (2H, Ar-H), 2.214 (s, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 168.91, 155.50, 150.99, 146.66, 129.62, 129.52, 129.44, 125.57, 124.25, 122.32, 121.09, 19.65. FT-Mass [$M + H^+$] (m/z) calcd. 331.14410, found 331.14434.

2. Measurements

2.1. NMR, and mass spectrometry

The nuclear magnetic resonance (NMR) spectra of the samples were dissolved in deuterated chloroform and analyzed under room temperature by using an Agilent Unity plus-400 spectrometer. Fourier-transform mass spectrometry was performed using a JEOL AccuTOF GCx-plus instrument.

2.2 UV-Visible absorption, and photoluminescence properties

The light absorption properties of the samples in dichloromethane (DCM) (concentration = 1×10^{-5} M) were measured using a PerkinElmer Lambda 35 UV-visible (UV-Vis) spectrometer. The photoluminescence (PL) spectra of samples in DCM (concentration = 1×10^{-5} M) were recorded using a Hitachi F-4500 spectrometer at an excitation wavelength of 330 nm.

2.3 Thermal properties

A Perkin Elmer DSC 6000A was used to determine the melting point (T_m) under nitrogen atmosphere with a scan rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 Simultaneous DTA-TGA device under nitrogen atmosphere at a heating rate of 15 °C min⁻¹; the samples analyzed had a mass of 3–5 mg. The thermal degradation temperature (T_d) was taken as the temperature at which 5% weight loss had occurred.

2.3 Cyclic voltammetry

Cyclic voltammetry (CV) was performed using a BioLogic SP-150 model at a scan rate of 100 mV s⁻¹ in the range of 0 to -2 V for the reduction potential and 0 to 1.5 V for the oxidation potential. All measurements were conducted at room temperature in DCM solution (concentration = 1 × 10⁻³ M) with a conventional three-electrode configuration, in which the three electrodes were a platinum working electrode, a platinum wire auxiliary electrode, and a Ag/Ag⁺ reference electrode.

2.5 Computational procedure

The electronic absorption spectra for the different compounds were calculated with time-dependent density functional theory at the MPW1PW91/6-31g* level of theory on the relaxed geometries optimized at the UB3LYP/6-31G* level of theory. Molecular orbital calculations were carried out using the Gaussian 03 suite of programs. The triplet state energy levels were also calculated at this level of theory.²

2.6. Photolysis experiment

Photolysis experiments of the selected photoinitiations (concentration = 1 × 10⁻⁵ M) in DCM as a solvent were performed and the results were recorded using a PerkinElmer Lambda 35 UV-Vis spectrometer. The absorption intensity of the solution was determined with various durations of exposure under LED@365 nm and LED@405 nm (Intensity = 50 mW cm⁻²).

2.7. ESR experiment

ESR experiments were conducted using a Bruker EMX Plus X-Band spectrometer. Ultra-high-pressure mercury (MUV-250U-L, λ = 250–450 nm, intensity = 5 mW) was selected as the radiation source used to generate radicals at room temperature under nitrogen atmosphere. The radicals were trapped by N-tert-Butyl-α-phenylnitron (PBN), and *tert*-butylbenzene as a solvent in accordance with a procedure described in the literature.³ The concentrations of PBN and oxime ester were 1 × 10⁻² M and 1 × 10⁻³ M respectively.

2.8. Fluorescence lifetime experiment

Fluorescence excited state lifetimes were determined using a time correlated single-photon counting system named HORIBA DeltaFlex with a HORIBA PPD-850 as detector. The excitation source was a HORIBA nanoLED-370 with an excitation wavelength of 367 nm and a pulse duration inferior to 1.4 ns. Fluorescence intensity decay profiles were recorded in DCM in a quartz cell. A silica colloidal solution LUDOX AS 30, 30 wt% suspension in H₂O was used to evaluate the impulse response function (IRF) of the apparatus.²

2.9. Photo-DSC experiment

The photopolymerization efficiency of the formulations was tested through photo-DSC analysis, performed using a Perkin Elmer DSC 6000 at 30 °C under nitrogen atmosphere (flow rate = 20 mL min⁻¹). A UV lamp (intensity = 180 or 50 mW cm⁻²; λ = 250–450 nm) or LED@365 nm (intensity = 50 mW cm⁻²) or LED@405 nm (intensity = 50 mW cm⁻²) was used as the radiation source. Oxime esters and TMPTA were mixed without additional solvent to obtain a photoinitiation system. Approximately 15 mg of a sample mixture (containing the hydrogen acceptor, hydrogen donor, and TMPTA under a certain weight ratio) was placed in an aluminum DSC pan, which was used to ensure the different formulations had similar thickness. Heat flow versus time curves were recorded to analyze the reaction of unsaturated moieties in the system during light irradiation. By integrating the area under the exothermic peak, the double bond conversion efficiency (DC; %) could be calculated using the following equation:⁴

$$DC = (\Delta Ht/n \times \Delta H_o^{\text{theor}}) \times 100\%,$$

where ΔHt is the total reaction heat enthalpy within the exposure time, and $\Delta H_o^{\text{theor}}$ is the theoretical reaction heat enthalpy of one acrylate for complete conversion. $\Delta H_o^{\text{theor}}$ was 86 kJ mol⁻¹.⁵ n is the number of acrylate unit. TMPTA monomer used in this study has three acrylate functional groups, thus, n is equal to 3.

Furthermore, the rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the equation $R_p = dC/dt$.⁶

2.10 RT-FTIR experiment

The photopolymerization kinetics of TA and EPOX were obtained by using real-time Fourier transform infrared spectroscopy (JASCO FTIR 6600). For the FRP of TA, the formulations were put in laminate between two propylene films (thickness ~ 25 μm) to reduce O₂ inhibition whereas they were placed on polypropylene films (under air) for the CP of EPOX. Decrease of the C=C double bond peak or the epoxide group band were continuously observed from 1581 to 1662 cm⁻¹ or from 768 to 825 cm⁻¹ respectively. The final acrylate function conversion of TA and the final epoxy function conversion of EPOX were obtained by using the following equation:²

$$FC (\%) = \frac{A_0 - A_t}{A_0} \times 100$$

Where FC is the final function conversion, A0 is the proportion of the peak area at 0 sec, and At is the portion of the peak area at t s. The prepared formulations were stirred in the dark for 24 h. All the polymerization experiments were performed by using the LED@405 nm at room temperature and the irradiation was initiated after $t = 10$ s.

2.11. DSC experiment

About 10 mg of TA containing 1 wt% PI was inserted into a 100 μ L aluminum crucible. Thermal polymerization was performed from 25 to 300 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C min^{-1} under nitrogen flow (100 mL min^{-1}). A Mettler Toledo DSC 1 differential scanning calorimeter was used for this purpose.

1. Z. H. Lee, F. Hammoud, A. Hijazi, B. Graff, J. Lalevee and Y. C. Chen, *Polym. Chem.*, 2021, **12**, 1286-1297.
2. A. Noon, F. Hammoud, B. Graff, T. Hamieh, J. Toufaily, F. Morlet-Savary, M. Schmitt, T. T. Bui, A. Rico, F. Goubard, S. Peralta, F. Dumur and J. Lalevee, *Adv. Mater. Technol.*, 2023, DOI: 10.1002/admt.202300205.
3. T. L. Huang, Y. H. Li and Y. C. Chen, *J. Polym. Sci.*, 2020, **58**, 2914-2925.
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6. S. X. Chen, C. Qin, M. Jin, H. Y. Pan and D. C. Wan, *J. Polym. Sci.*, 2021, **59**, 578-593.

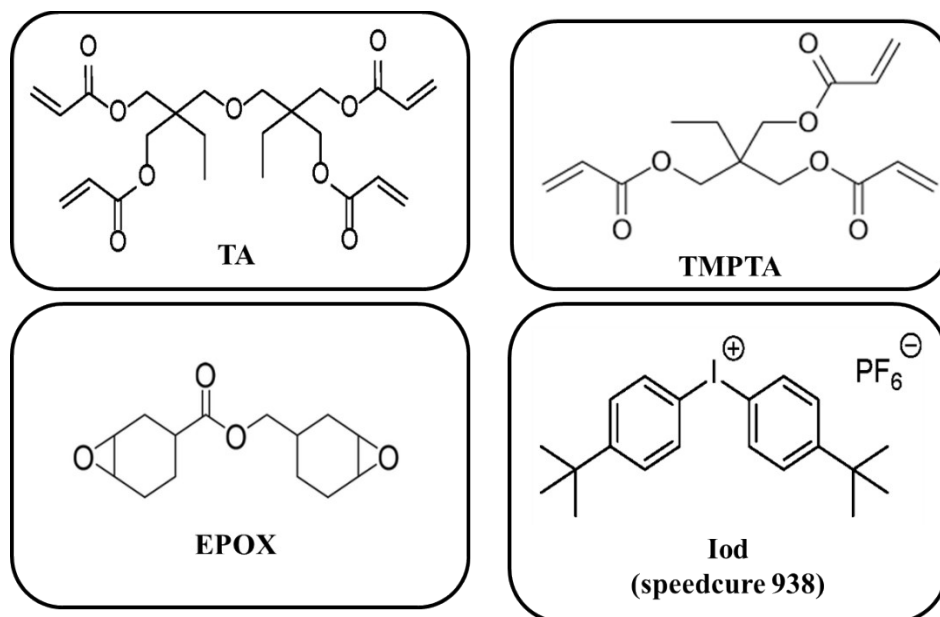


Fig. S1 Chemical structures of TMPTA, TA, EPOX and Iod.

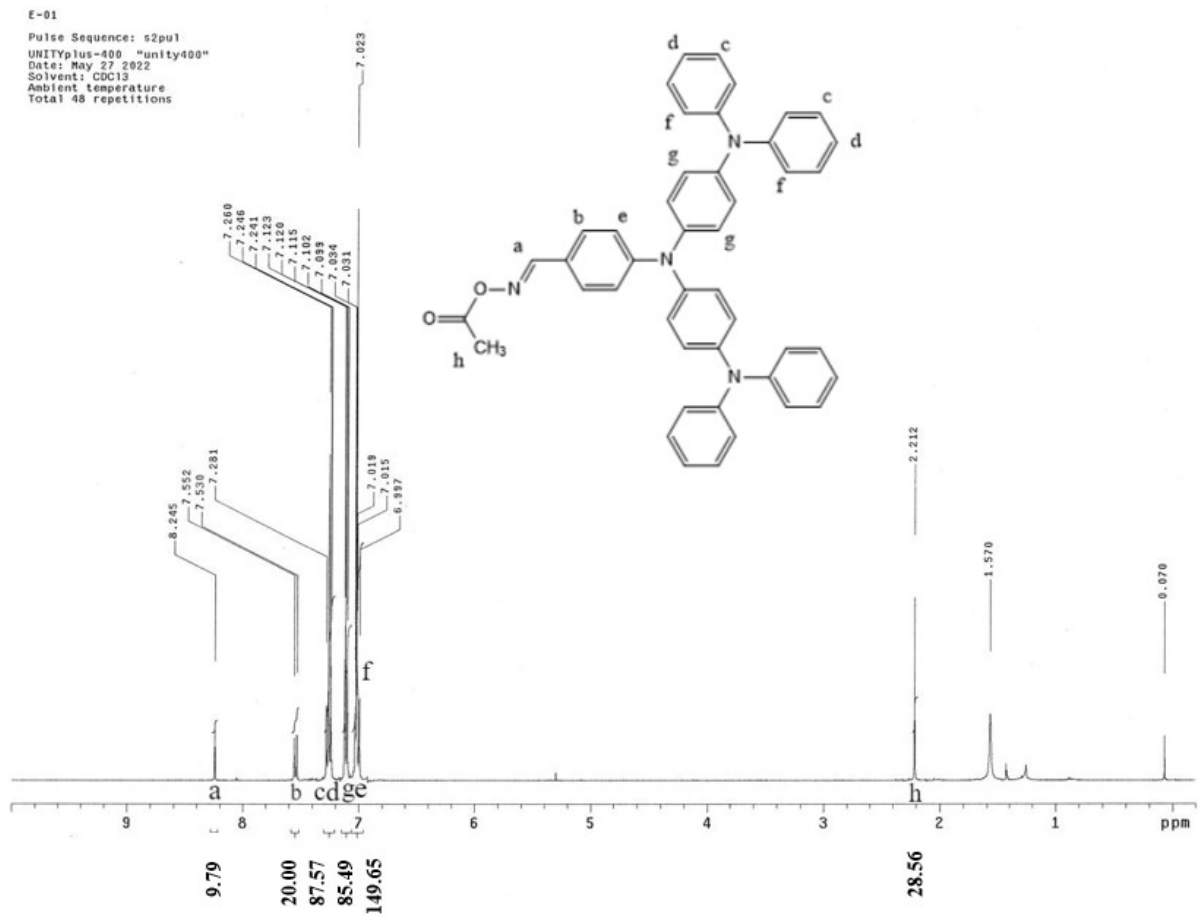


Fig. S2 ¹H NMR of the TPA-DP.

CZE3

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Date: Dec 6 2021
Solvent: cdcl3
Ambient temperature
Total 32 repetitions

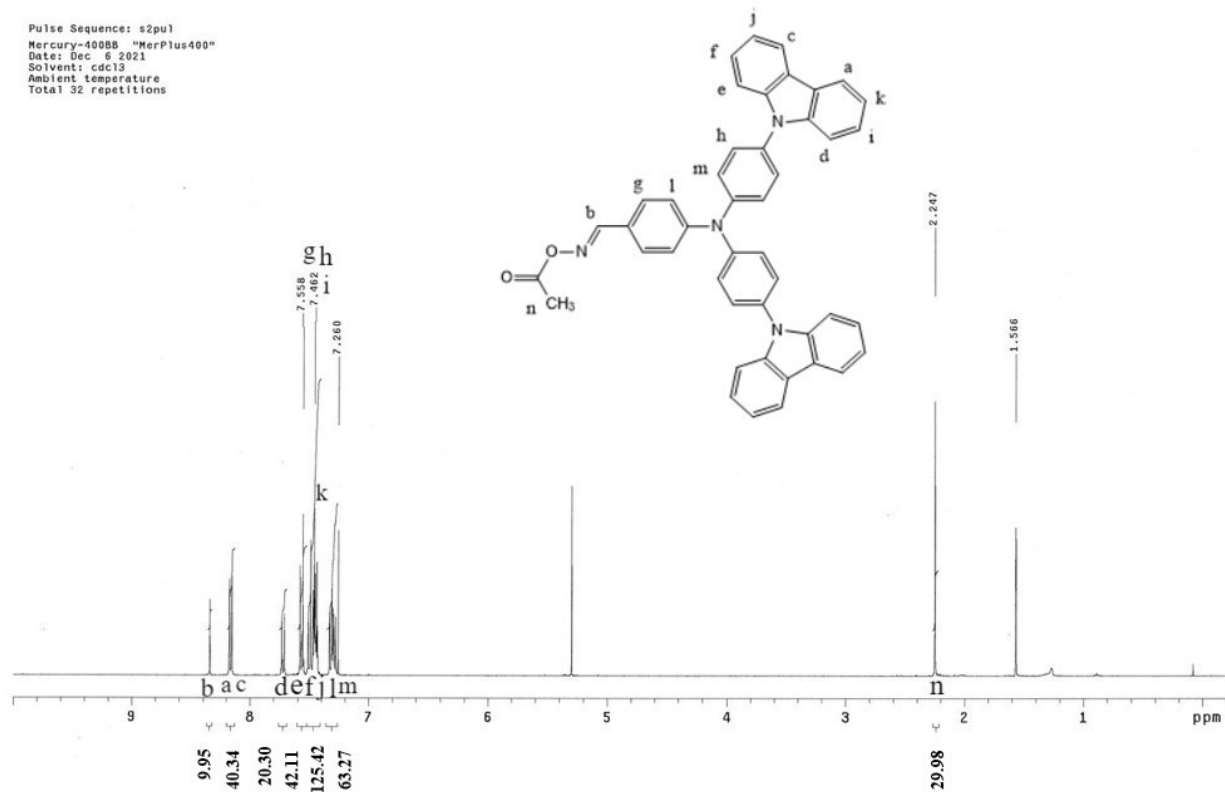


Fig. S3 ¹H NMR of the TPA-CZ.

NSF3
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Date: Jan 18 2022
Solvent: CDCl3
Ambient Temperature
Total 40 repetitions

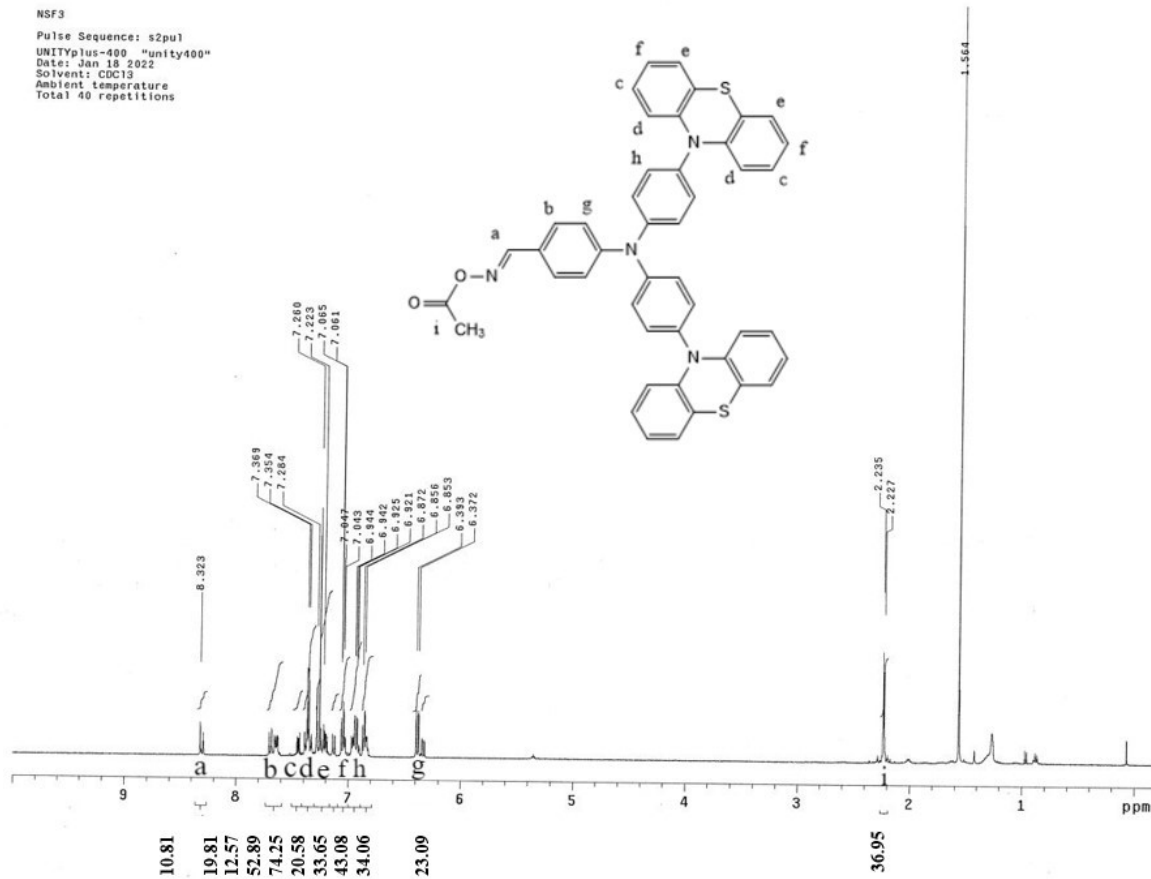


Fig. S4 ¹H NMR of the TPA-PT.

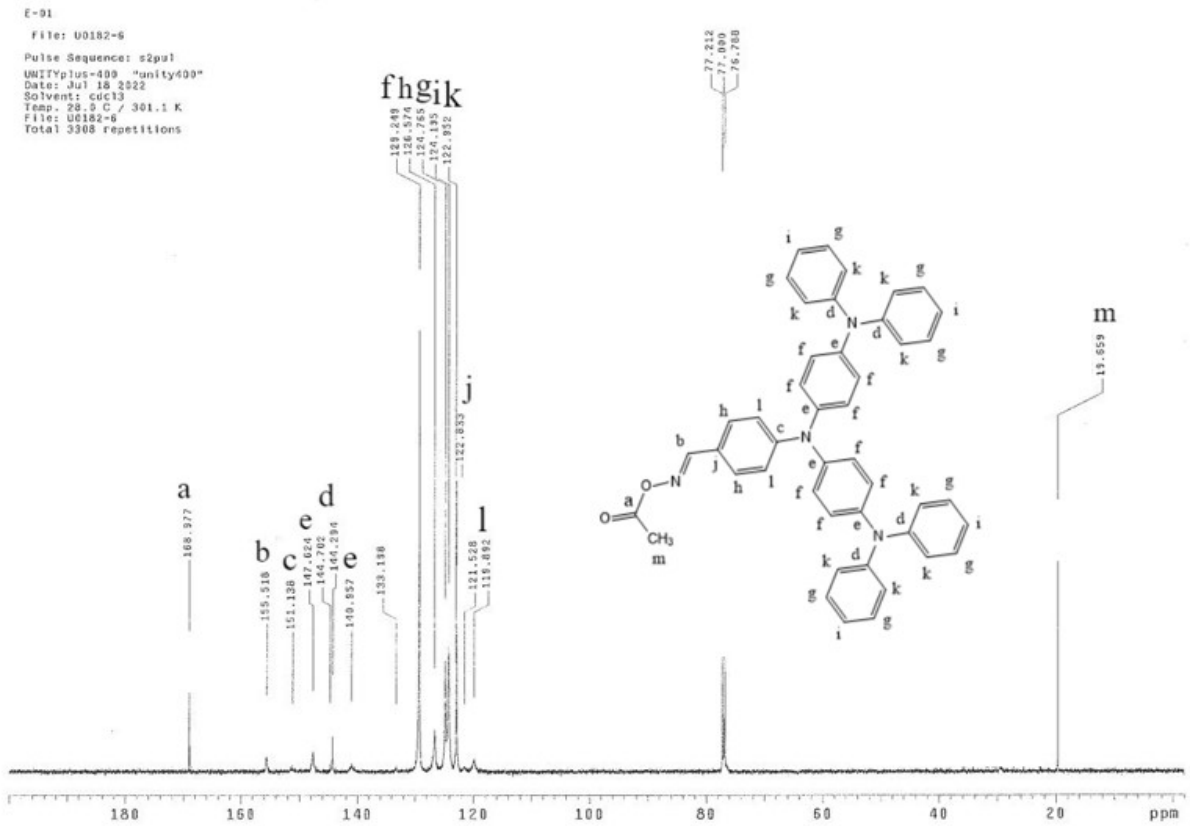


Fig. S5 ¹³C NMR of the TPA-DP.

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Solvent: CDCl3
Ambient temperature
Total 1216 repetitions

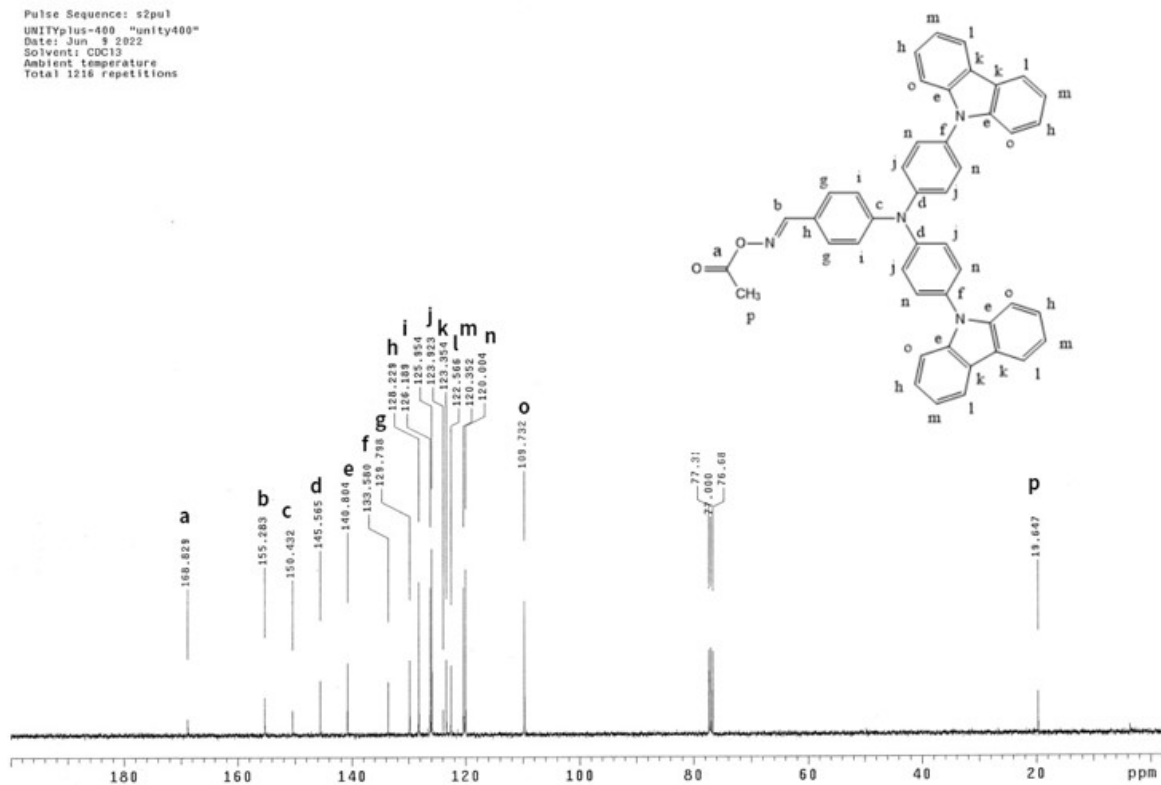


Fig. S6 ¹³C NMR of the TPA-CZ.

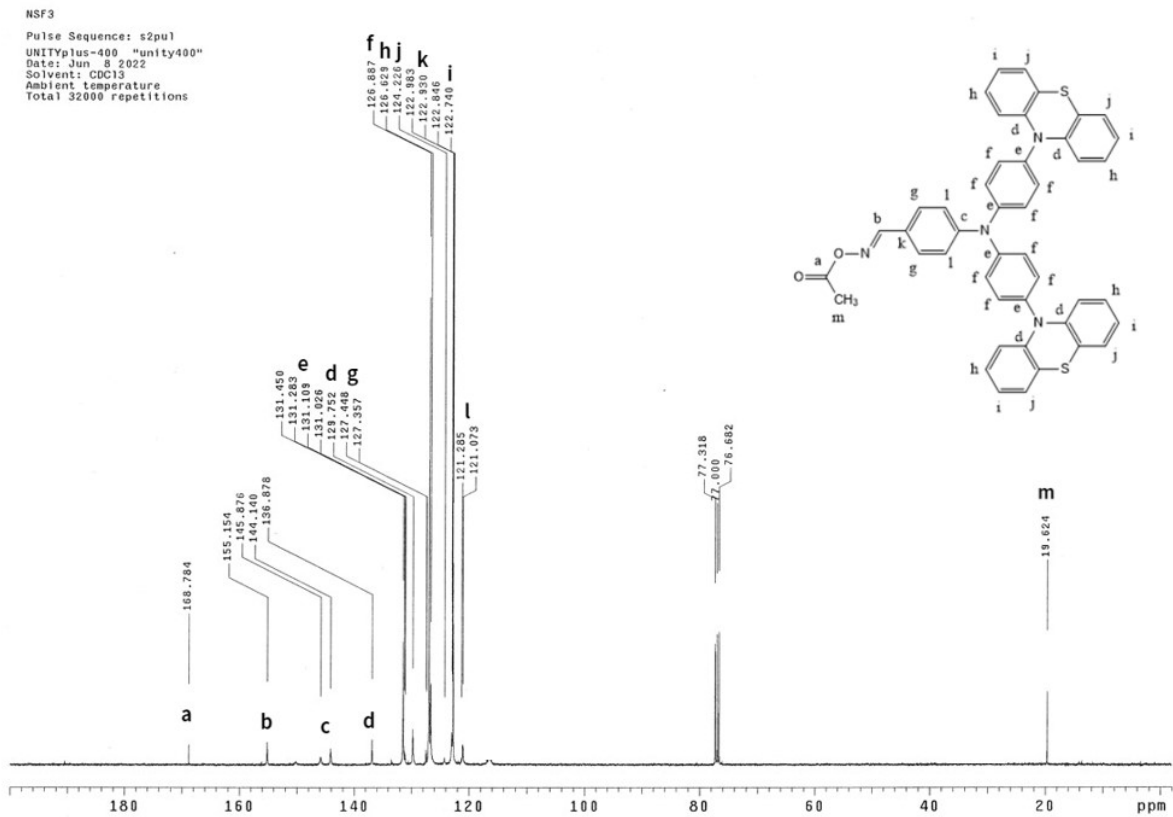
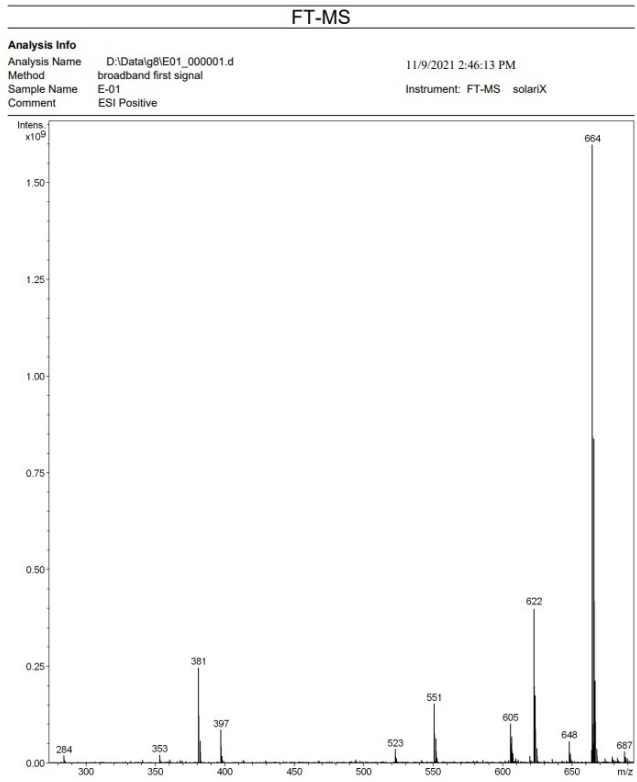
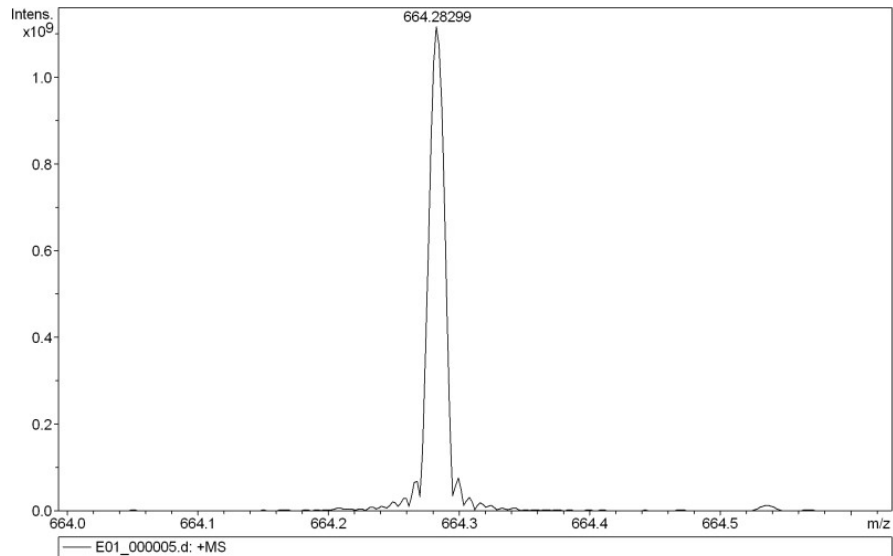


Fig. S7 ¹³C NMR of the TPA-PT.



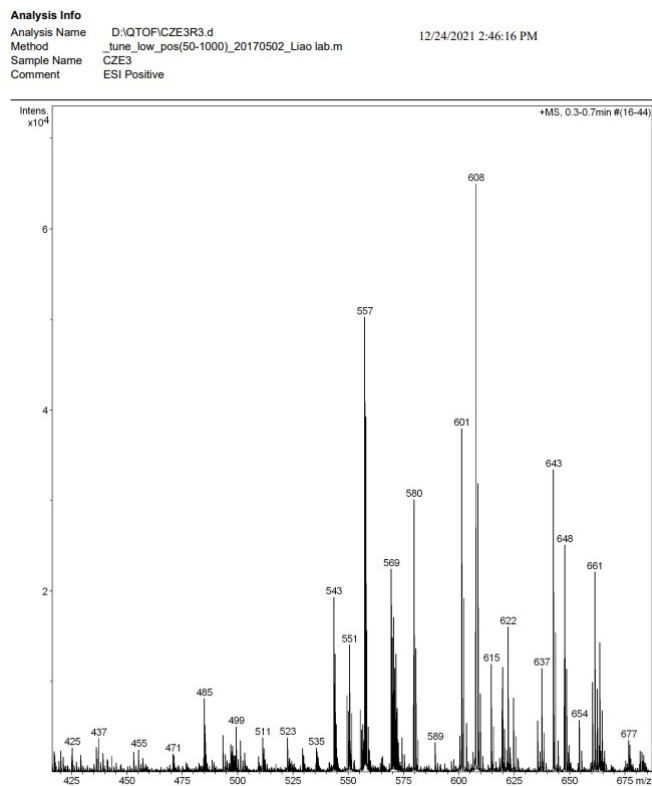
Mass Spectrum SmartFormula Report

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 Sample Name: E-01
 Comment: ESI Positive
 11/9/2021 2:49:01 PM
 Operator: YU HSIAO-CHING
 Instrument: BRUKER FT-MS solarix



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
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Fig. S8 HR-MS of the TPA-DP.



Mass Spectrum SmartFormula Report

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 Instrument: BRUKER micrOTOF-Q

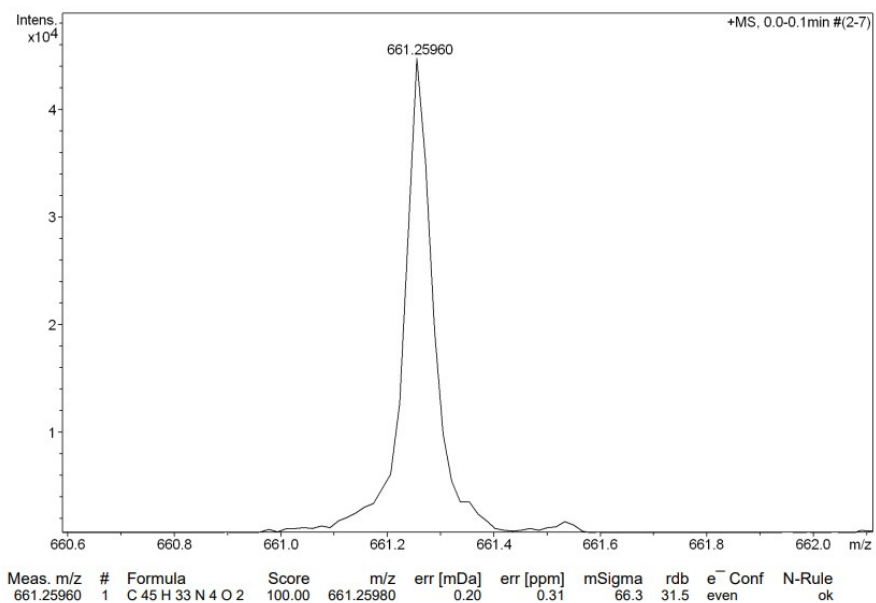
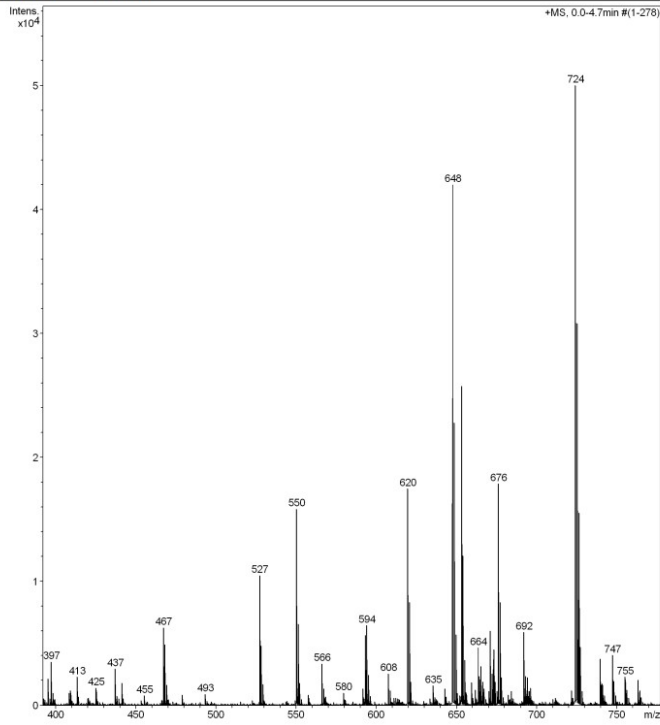


Fig. S9 HR-MS of the TPA-CZ.

Analysis Info

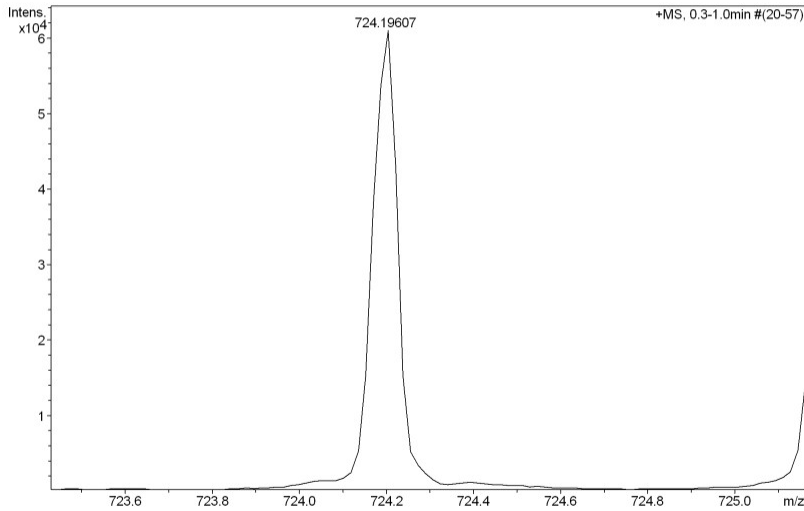
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Comment ESI Positive



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name NSF3 Instrument: BRUKER micrOTOF-Q
Comment ESI Positive



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Fig. S10 HR-MS of the TPA-PT.

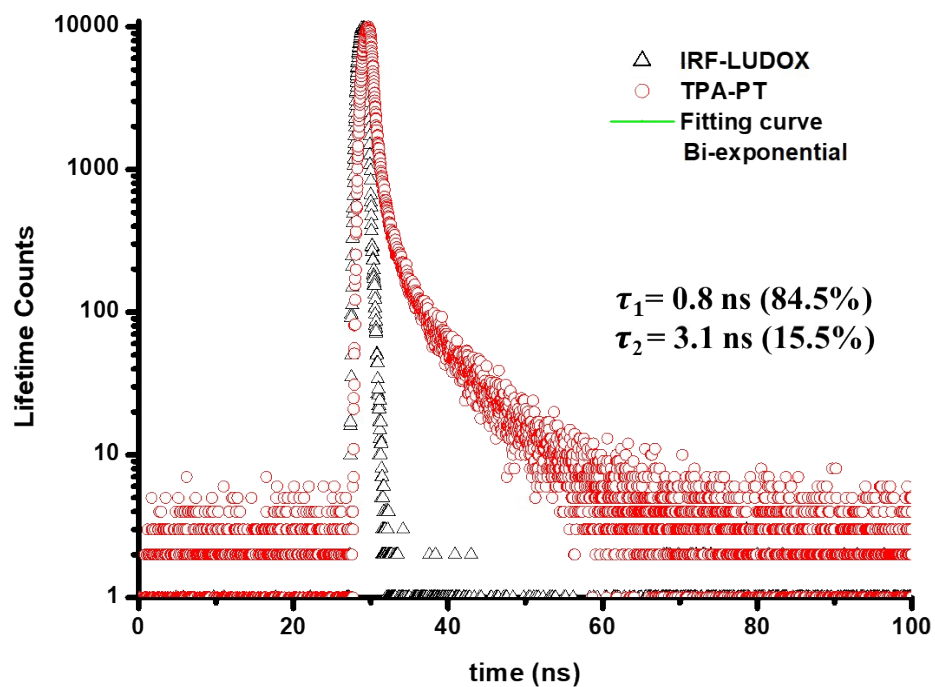


Fig. S11 Time correlated single-photon counting of TPA-PT in acetonitrile, $\lambda_{\text{ex}} = 367 \text{ nm}$, $\lambda_{\text{em}} = 492 \text{ nm}$.

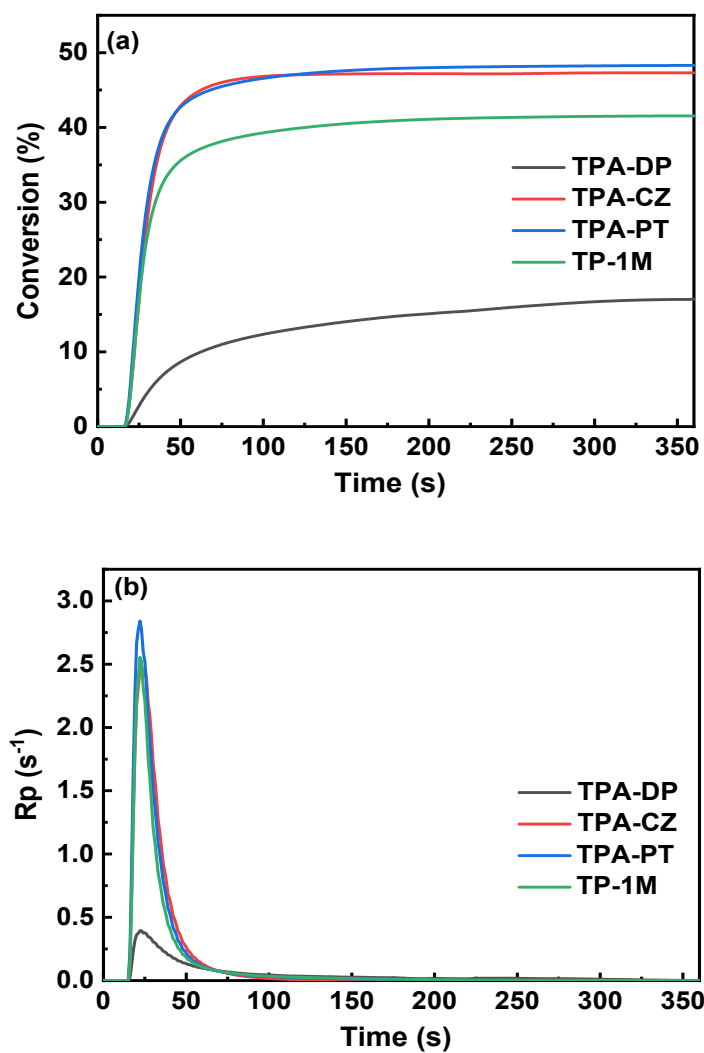


Fig. S12 (a) Conversion versus time, and (b) R_p versus time of TMPTA photopolymerization initiated by oxime esters (2 wt%) under UV light irradiation ($I = 180 \text{ mW cm}^{-2}$). The irradiation starts at $t = 24 \text{ s}$.

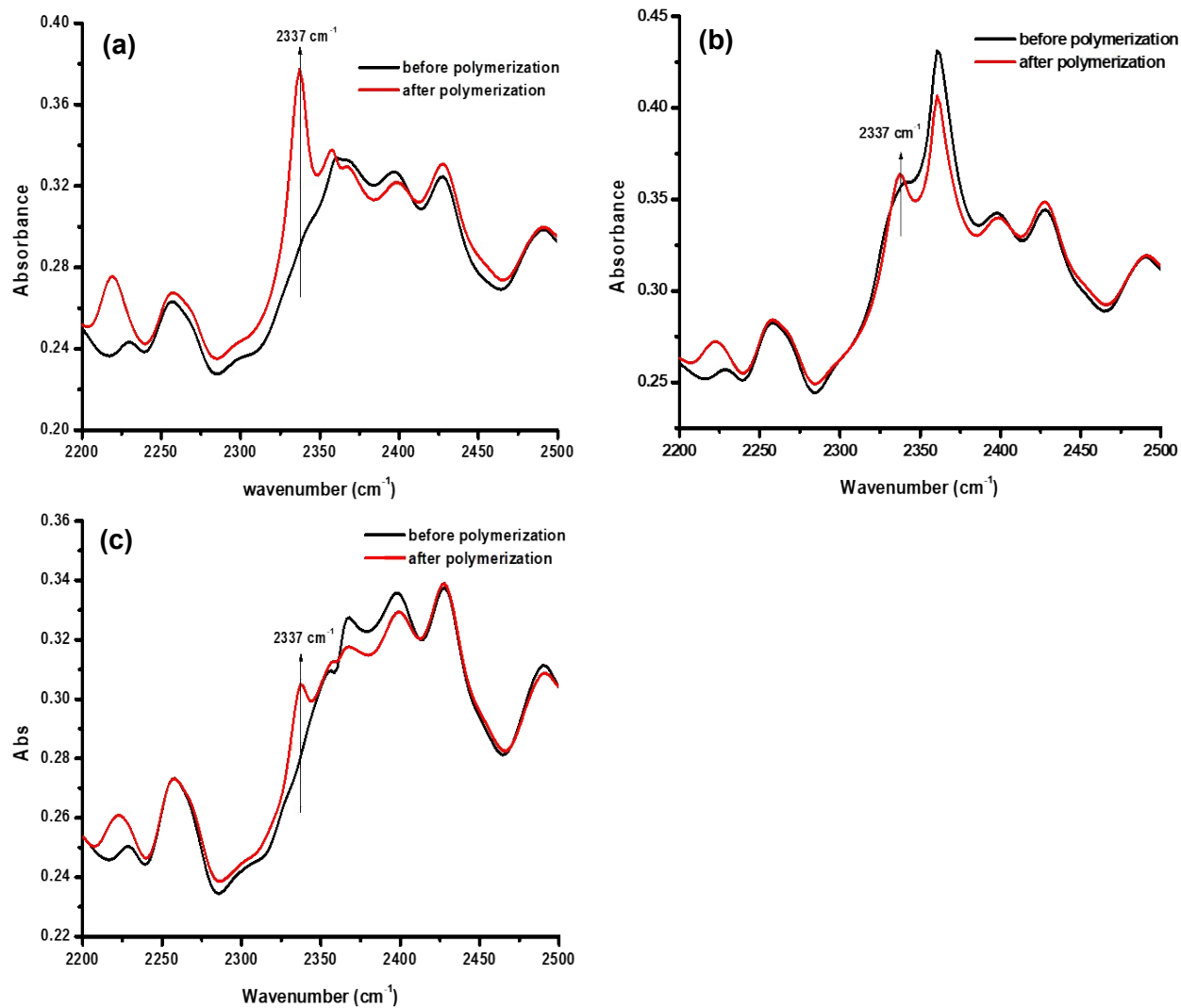


Fig. S13 Detection of CO₂ released during photopolymerization using (a) TP-1M, (b) TPA-CZ, and (c) TPA-PT; PI (2% w/w) in TA (thin film polymerization @ 405 nm in laminate).

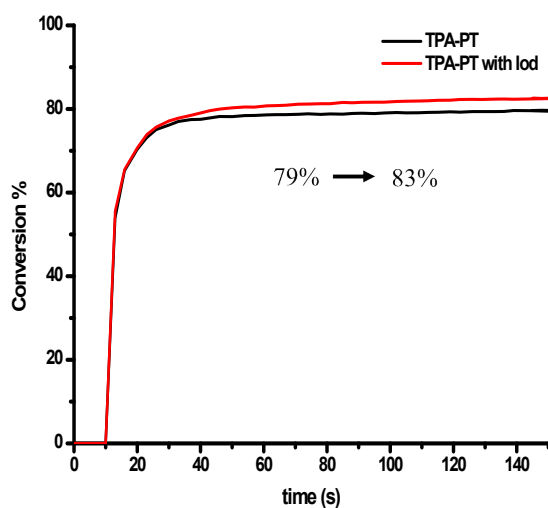
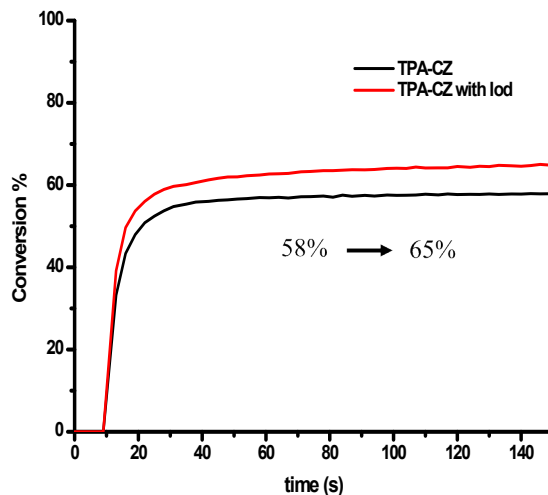
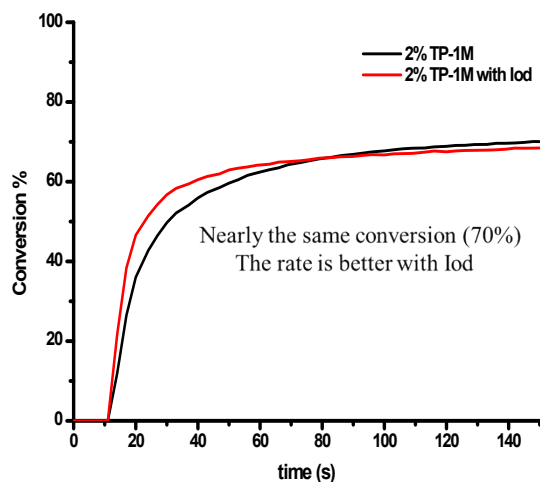


Fig. S14 Photopolymerization profiles of TA (acrylate function conversion vs irradiation time) in laminate (thickness=25 μ m) upon exposure to LED (λ =405 nm) in the presence of PI/Iod (2%/1% w/w) or PI (2 wt%). The irradiation starts at 10 s.

Table S1. Photo-DSC results derived from 2 wt% of oxime esters under TMPTA monomer^a

PI^b	Conversion (%)	ΔH_t (kJ mol ⁻¹) ^c	H_{max} (mW mg ⁻¹) ^d	Rp_{max} (s ⁻¹) ^e	T_{max} (s) ^f
TPA-DP	17	44	51	0.39	22
TPA-CZ	47	122	324	2.50	24
TPA-PT	48	125	384	2.84	21
TP-1M	42	107	337	2.55	22

^a. Measured with 180 mW cm⁻² of UV light (λ : 250-450 nm) for 6 min.

^b Photo-DSC of the **PIs** /TMPTA at weight ratios of **PIs** : TMPTA = 2 : 98

^c. ΔH_t is the totally reaction heat enthalpy within 5 min.

^d. H_{max}: maximum heat flow values.

^e. Rp_{max}: maximum rate of polymerization.

^f. T_{max}: time at maximum heat flow.