Simple thiophene-bridged D-π-A type chromophores for DSSCs: A comprehensive study on their sensitization and co-sensitization properties

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1. Materials and methods

The starting materials such as 4-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 1-bromododecane, thiophene-2-acetonitrile, cyanoacetic acid, and barbituric acid were procured from Sigma-Aldrich, Alfa Aesar, and Spectrochem companies. All the solvents used in the reactions were of synthetic grade (Merck, Loba Chemie, and Spectrochem companies) and they were purified by further drying and distillation process. All the reactions were carried under an inert (argon) atmosphere and the reaction completion was monitored by the TLC technique. The designed dyes were synthesized by using standard synthesis protocol. The target dyes and their intermediates were purified using recrystallization or column chromatographic separation techniques. The melting points of synthesized molecules were recorded using the Stuart SMP10 digital melting point apparatus. ^{1}H NMR (400 MHz) spectra of synthesized molecules were recorded on the Bruker Avance (III) 400 MHz instrument by using DMSO-d_6 as a solvent. The chemical shift (δ) was expressed in parts per million (ppm) relative to the solvent residual peak with tetramethylsilane (TMS) as an internal standard and coupling constant (J) is expressed in Hz. The LCMS and elemental analysis of the synthesized dyes $\mathbf{T_{1\text{-}4}}$ were obtained from the LC-MS6410Q (Agilent Technologies) and Flash EA1112 CHNS elemental analyzer (Thermo Scientific), *respectively*. FT-IR spectra were obtained using the Bruker FTIR Alpha spectrometer. Also, Thermogravimetric analysis (TGA) was carried out using the Perkin Elmer TGA4000 analyzer, at the heating rate of 10 °C min^{-1} under the nitrogen atmosphere. Similarly, differential scanning calorimetry (DSC) studies were carried out using the NETZSCH DSC 404F1 analyzer. The UV-Vis absorption spectra and photoluminescence spectra of $\mathbf{T_{1\text{-}4}}$ in *N,N*-dimethyl formamide (DMF) solvent were recorded at room temperature by using the Analytik Jena SPECORD S 600 and Jasco FP 6200 spectrophotometers, *respectively*. Furthermore, in order to assess their experimental GSOP and ESOP values, the CV (cyclic voltammetry) measurements were performed in anhydrous acetonitrile solution with 0.1M tetrabutylammonium hexafluorophosphate [TBA] [PF_6] as a supporting electrolyte at a scan rate of 100 mVs^{-1}. The theoretical simulations, *viz.* density functional theory (DFT) and time-dependent density functional theory (TD-DFT), were performed for all the final molecules using the Turbomole V7.2 software package.

Photoelectrochemical measurements

The DSSC devices sensitized with new $\mathbf{T_{1-4}}$ dyes were fabricated by using the doctor blade technique. Similarly, DSSCs were constructed employing the dyes $\mathbf{T_{1-4}}$ as co-sensitizers along with Ru-based **MH-12**dye and chenodeoxycholic acid (CDCA) as a co-adsorbent. Further, the J-V (Current-Voltage) characteristics of fabricated devices were measured using solar simulator Oriel SOL3A connected to Keithley 2400 source meter. Further, incident photon conversion efficiency (IPCE) spectra of all the fabricated devices with $\mathbf{T_{1-4}}$ were recorded using the QEX10 PV measurement system. Finally, electrochemical impedance spectra (Nyquist and Bode plots) for the fabricated devices were measured with Bio-Logic SP-150 potentiostat using a solar simulator under the illumination of standard 1.5 G light source.

2. Synthetic methods

General method for synthesis of intermediates **2a-b**

A mixture of 4-hydroxybenzaldehyde or 3,4-dihydroxybenzaldehyde (**1**, 1 eq) was dissolved in a minimum amount of DMF and stirred for 0.5 h under an argon atmosphere at room temperature. Later potassium carbonate (3 eq) is added to the above mixture. Further, 1-bromododecane (1.2 eq) was added to the above reaction mixture and was heated with stirring at 80 ^{o}C for 12 h. The reaction progress was monitored using thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled, and poured into ice-cold water and extracted with dichloromethane (30 mL x 3). The combined organic layer was dried using sodium sulphate and the solvent was removed under reduced pressure. Finally, the crude product was purified by the column chromatography method using 100-200 silica mesh (pet ether: ethyl acetate, 3:1, as eluent) to obtain the pure product as a colorless liquid. Yield: 89-91%.

General method for synthesis of intermediates **3a-b**

Intermediate **2a** or **2b** (1 eq) and thiophene-2-acetonitrile (1.2 eq) was slowly added to the round-bottomed flask containing freshly prepared sodium methoxide (1.8 eq, 50 mL) solution. The reaction mass was stirred at room temperature under argon atmosphere for 8 h. The bright yellow precipitate formed was filtered off, washed with cold methanol and finally, it was recrystallized from chloroform to give fine yellow solid of **3a-b**.

(E)-3-(4-(Dodecyloxy)phenyl)-2-(thiophen-2-yl)acrylonitrile (**3a**)

1H NMR (400 MHz, DMSO-d6, δ ppm): 7.84-7.82 (d, 1H), 7.33-7.26 (m, 4H), 7.06 (s, 1H), 6.96-6.94 (d, 2H), 4.03-4.00 (t, 2H), 1.82-1.27 (m, 20H), 0.88-0.87 (t, 3H). **FT-IR(ATR), υ** cm^{-1}: 2850 (C-H stretch), 2218 (C≡N stretch), 1510 (C=C). Melting point: 176 °C. Yield: 83%.

(E)-3-(3, 4-Bis (dodecyloxy)phenyl)-2-(thiophen-2-yl)acrylonitrile (**3b**)

1H NMR (400 MHz, DMSO-d6, δ ppm): 7.58 (s, 1H), 7.33-7.31 (m, 4H), 7.06 (s, 1H), 6.91-6.89(d, 1H), 4.09-4.06 (t, 4H), 2.17-2.15 (d, 2H), 1.86-1.83 (d, 2H), 1.54-1.26(m, 36H), 0.89-0.86 (t, 6H). **FT-IR(ATR), υ** cm^{-1}: 2851 (C-H stretch), 2208 (C≡N stretch), 1599 (C=C). Melting point: 189 °C. Yield: 81%.

General method for synthesis of intermediates **4a-b**

DMF (5 eq) and phosphorous oxychloride (5 eq) was mixed under argon atmosphere and stirred at –3 to 4 ^{o}C for 30 minutes in order to get white colored Vielsmeier salt. To this salt, the intermediate **3a** or **3b** (1 eq) in dichloroethane (2-3 mL) was added and stirring was continued at room temperature for 12 h. After completion of the reaction, the reaction mass was poured into ice-cold water and subsequently basified by using 5M NaOH solution. The precipitated solid was filtered and collected. The crude product was further purified by column chromatography (100-200 mesh and Hexane: EtOAc, 3:1 eluent) and finally, it was recrystallized from ethanol to get the pure dark orange-colored solid **4a-b**.

(E)-3-(4-(Dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**4a**)

1H NMR (400 MHz, DMSO-d6, δ ppm): 9.86 (s, 1H), 7.84-7.82 (d, 1H), 7.69 (s, 1H), 7.33-7.26 (m, 2H), 7.37-7.36 (d, 2H), 6.96-6.94 (d, 1H), 4.03-4.00 (t, 2H), 1.82-1.27 (m, 20H), 0.88-0.87 (t, 3H). **FT-IR(ATR), υ** cm^{-1}: 3057-2712 (C-H stretch), 2212 (C≡N stretch), 1669 (C=O), 1589 (C=C). Melting point: 196 °C. Yield: 83%.

(E)-3-(3, 4-Bis (dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**4b**)

1H NMR (400 MHz, DMSO-d6, δ ppm): 9.86 (s, 1H), 7.70-7.69 (d, 1H), 7.69-7.63 (d, 1H), 7.45 (s, 1H), 7.40-7.39 (d, 1H), 7.37-7.36 (d, 1H), 6.91-6.89(d, 1H), 4.08-4.04 (t, 4H), 1.85-1.81 (m, 6H), 1.49-1.45 (m, 6H), 1.35-1.25 (m, 28H), 0.86-0.85 (t, 6H). **FT-IR(ATR), υ** cm^{-1}: 3042 (C-H stretch), 2208 (C≡N stretch), 1665 (C=O), 1595 (C=C). Melting point: 208 °C. Yield: 79%.

General method for synthesis of dyes $\mathbf{T_{1-2}}$

A mixture of intermediate **4a**, *3-(4-(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile* or **4b**, *3-(3,4-bis(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile* (1 eq), cyanoacetic acid (1.2 eq), and ammonium acetate (10 eq) and glacial acetic acid (10-15 mL) was taken in an RB flask and refluxed for 12 h under argon atmosphere. The completion of the reaction was monitored using the TLC technique. After its completion, the reaction mixture was cooled to room temperature and was poured into ice-cold water. The solid obtained was filtered, washed with cold water, and finally, dried. The crude product was recrystallized from absolute methanol to get the pure product $\mathbf{T_{1-2}}$.

(E)-2-Cyano-3-(5-((E)-1-cyano-2-(4-(dodecyloxy)phenyl)vinyl)thiophen-2-yl)acrylicacid ($\mathbf{T_1}$)

Bright red solid, Yield: 73%, Melting point: 244-246 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d6, δ ppm): 11.33 (s, 1H), 8.48 (s, 1H), 8.18-8.17 (d, 1H), 8.07 (s, 1H), 8.02-8.00 (d, 2H), 7.65-7.64 (d, 1H), 7.13-7.11 (d, 2H), 4.08-4.00 (t, 2H), 1.75-1.24 (m, 20H), 0.86-0.83 (t, 3H). Anal. Calcd. for $C_{29}H_{34}N_2O_3S$: C, 70.99; H, 6.91; N, 5.71 and found C, 71.02; H, 6.87; N, 5.74. **FT-IR(ATR), υ** cm^{-1}: 2923, 2850 (C-H stretch), 2208 (C≡N stretch), 1664 (C=O stretch), 1599, 1510 (C=C), 1179 (C-N stretch). **Mass (m/z):** 490.23; Obtained (M-H): 489.10.

(*E)-3-(5-((E)-2-(3,4-Bis(dodecyloxy)phenyl)-1-cyanovinyl)thiophen-2-yl)-2-cyanoacrylicacid* ($\mathbf{T_2}$).

Dark red solid, Yield: 69%. Melting point: 296-298 ^{o}C. **^{1}H NMR** (400 MHz, DMSO-d6, δ ppm): 8.31 (s, 1H), 8.16 (s, 1H), 7.70 (s, 1H), 7.60-7.49 (d, 2H), 7.32-7.12 (d, 2H), 4.25-4.00 (t, 4H), 1.75-1.25 (m, 40H), 0.85-0.65 (t, 6H). Anal. Calcd. for $C_{41}H_{58}N_2O_4S$: C, 72.96; H, 8.66; N, 4.15; and found C, 73.00; H, 8.63; N, 4.16. **FT-IR(ATR), υ** cm^{-1}: 2925, 2851(C-H stretch), 2208 (C≡N stretch), 1664 (C=O stretch), 1599, 1510 (C=C), 1180 (C-N stretch). **Mass (m/z):** 674.41; Obtained (M-H): 673.

General method for synthesis of dyes $\mathbf{T_{3-4}}$

A mixture of intermediate **4a**, *3-(4-(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile* or intermediate **4b**, *3-(3,4-bis(dodecyloxy)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile* (1 eq) was dissolved in 10-15 mL of absolute methanol and to this mixture 1.2 eq of an active methylene compound like cyanoacetic acid or barbituric acid (anchor) was added under argon atmosphere and heated at 60 ^{o}C with stirring for 10 h. After completion of

the reaction, the content was cooled to room temperature and precipitated solid was filtered, washed with cold methanol and collected. It was further recrystallized from $CHCl_3$-hexane mixture to get a pure product.

(E)-3-(4-(Dodecyloxy)phenyl)-2-(5-((2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)methyl)thiophen-2-yl) acrylonitrile (**T_3**).

Bright red solid, Yield: 74%. Melting point: 340-342^oC. **^{1}H NMR** (400 MHz, DMSO-d_6, δ ppm): 11.34 (s, 2H), 8.48 (s, 1H), 8.18-8.17 (d, 1H), 8.07 (s, 1H), 8.02-8.00 (d, 2H), 7.65-7.64 (d, 1H), 7.13-7.11 (d, 2H), 4.09-4.06 (t, 2H), 1.76-1.75 (m, 2H), 1.73-1.69 (m, 2H), 1.41-1.39 (m, 16H), 0.86-0.83 (t, 3H).Anal. Calcd. for $C_{30}H_{35}N_3O_4S$: C, 67.52; H, 6.61; N, 7.87; and found C, 67.55; H, 6.63; N, 7.85. **FT-IR(ATR), υ** cm^{-1}: 3203 (N-H stretch), 2944, 2835 (C-H stretch), 2320 (C≡N stretch), 1595, 1522, 1494 (C=C), 1180 (C-N stretch). **Mass (m/z):** 533.23; Obtained (M-H): 532.10.

(E)-3-(3,4-Bis(dodecyloxy)phenyl)-2-(5-((2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene) methyl) thiophen-2-yl)acrylonitrile (**T_4**).

Blackish brown colored solid, Yield: 71%; Melting point: 338-340^oC. **^{1}H NMR** (400 MHz, DMSO-d6, δ ppm): 11.34 (s, 2H), 8.47 (s, 1H), 8.00-7.98 (d, 3H), 7.61-7.60 (d, 1H), 7.13-7.11 (d, 2H), 4.09-4.06 (t, 4H), 1.74-1.71 (m, 4H), 1.41-1.24 (m, 36H), 0.86-0.84 (t, 6H). Anal. Calcd. for $C_{42}H_{59}N_3O_5S$: C, 70.26; H, 8.28; N, 5.85; and found C, 70.28; H, 8.30; N, 5.81.**FT-IR(ATR), υ** cm^{-1}: 3192 (N-H stretch), 2840 (C-H stretch), 2322 (C≡N stretch), 1529, 1495 (C=C), 1183 (C-N stretch). **Mass (m/z):** 718; Obtained (M-H): 717.

3. Structural characterization

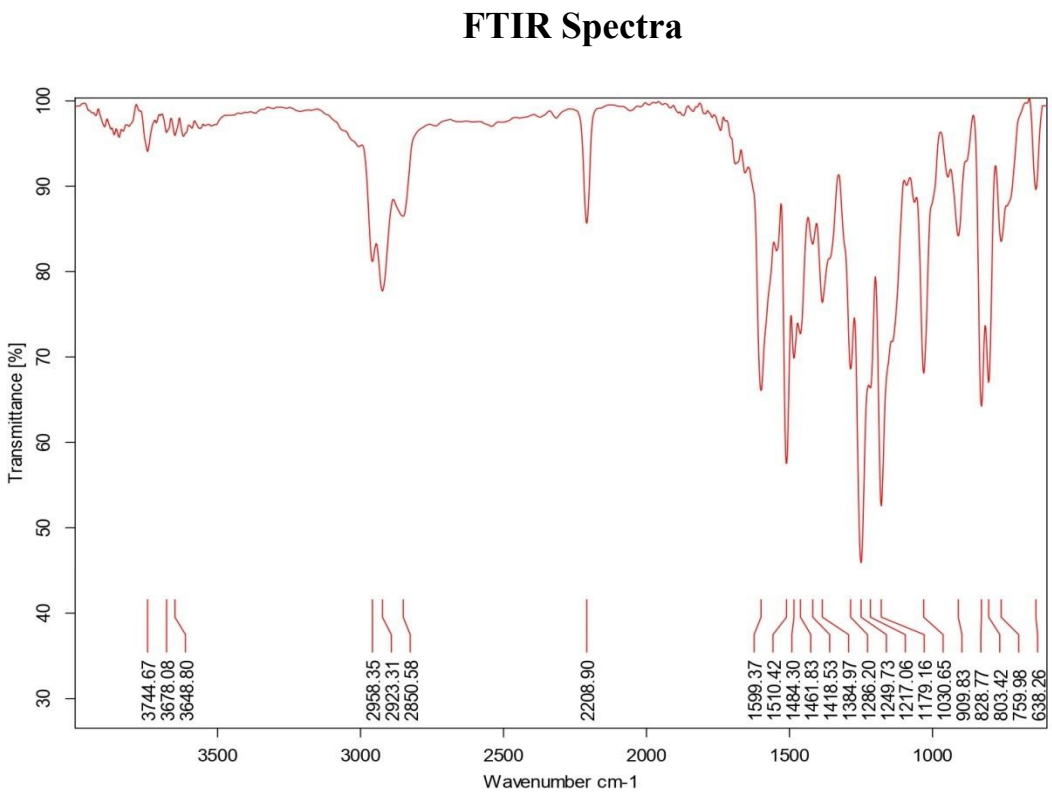


Figure S1. FT-IR spectrum of $\mathbf{T_1}$

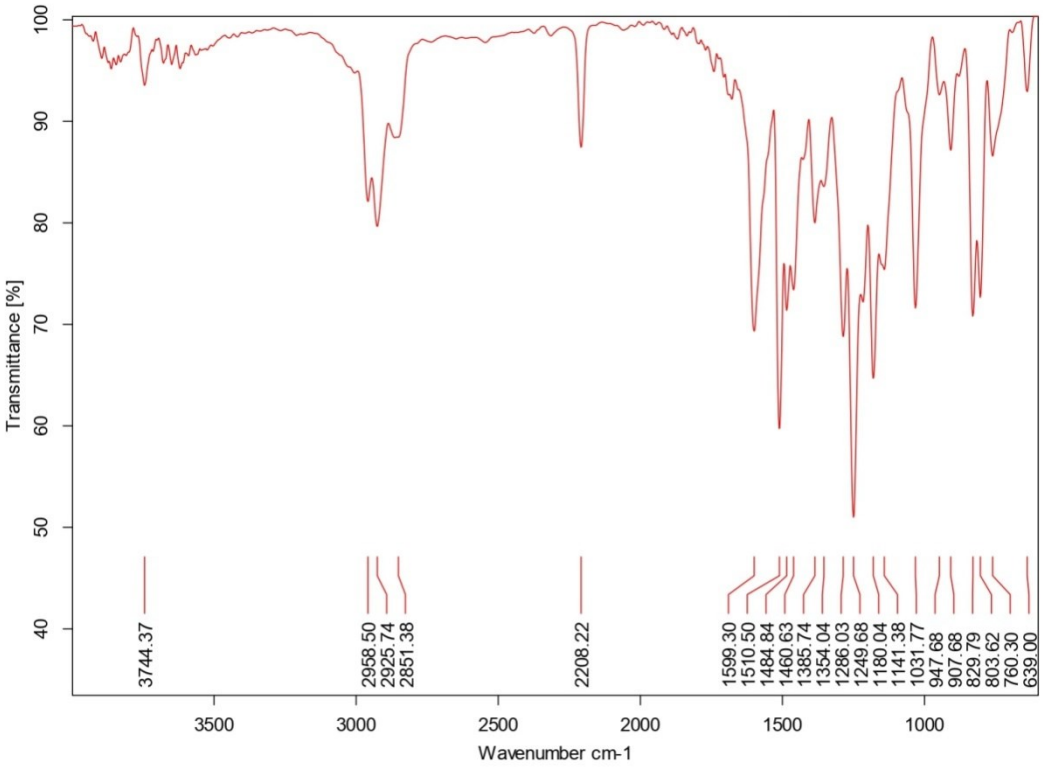


Figure S2. FT-IR spectrum of $\mathbf{T_2}$

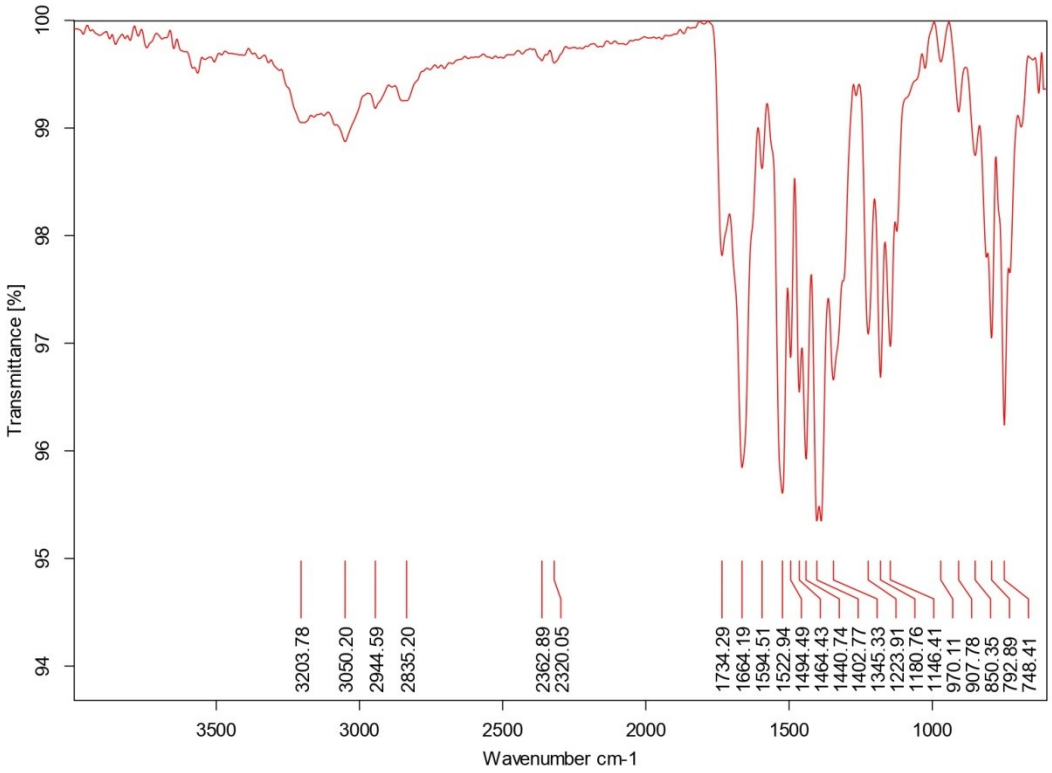


Figure S3. FT-IR spectrum of $\mathbf{T_3}$

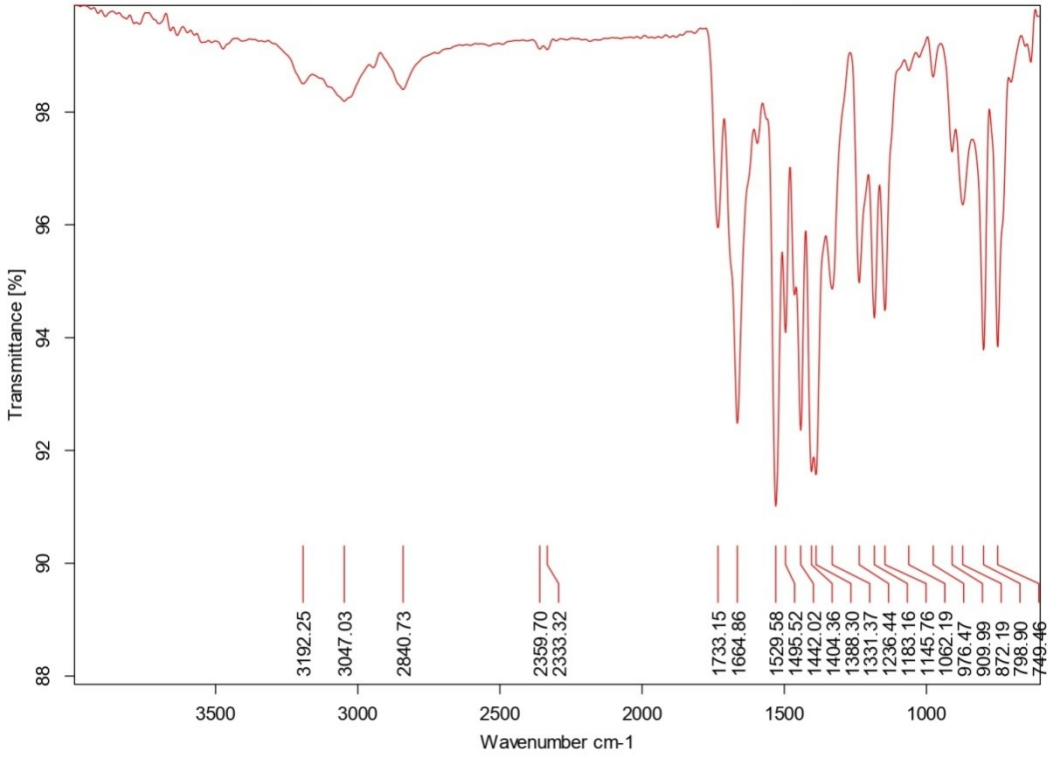


Figure S4. FT-IR spectrum of $\mathbf{T_4}$

^{1}H-NMR spectra

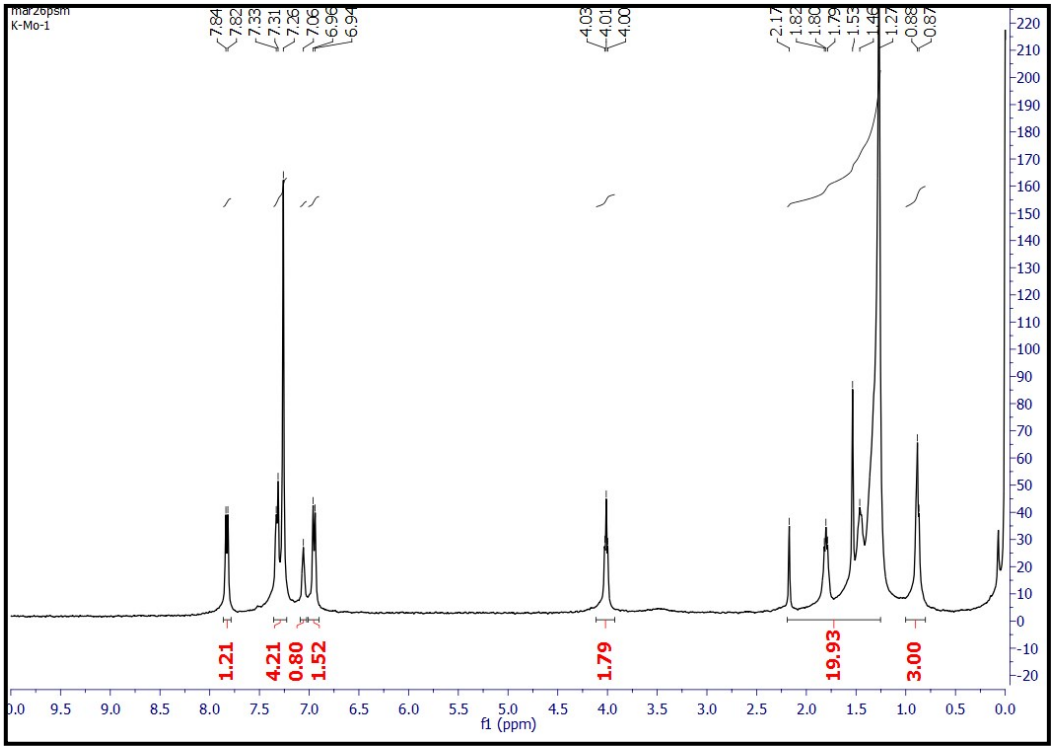


Figure S5. ^{1}H-NMR spectrum of intermediate **3a** recorded in DMSO-d_6

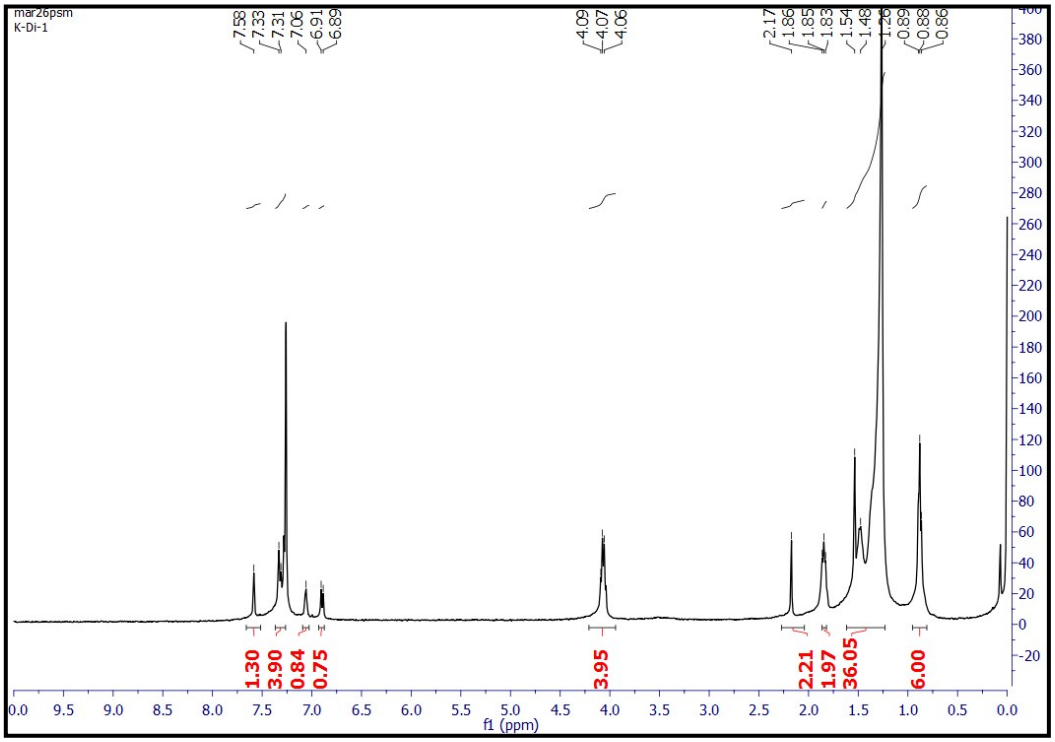


Figure S6. ^{1}H-NMR spectrum of intermediate **3b** recorded in DMSO-d_6

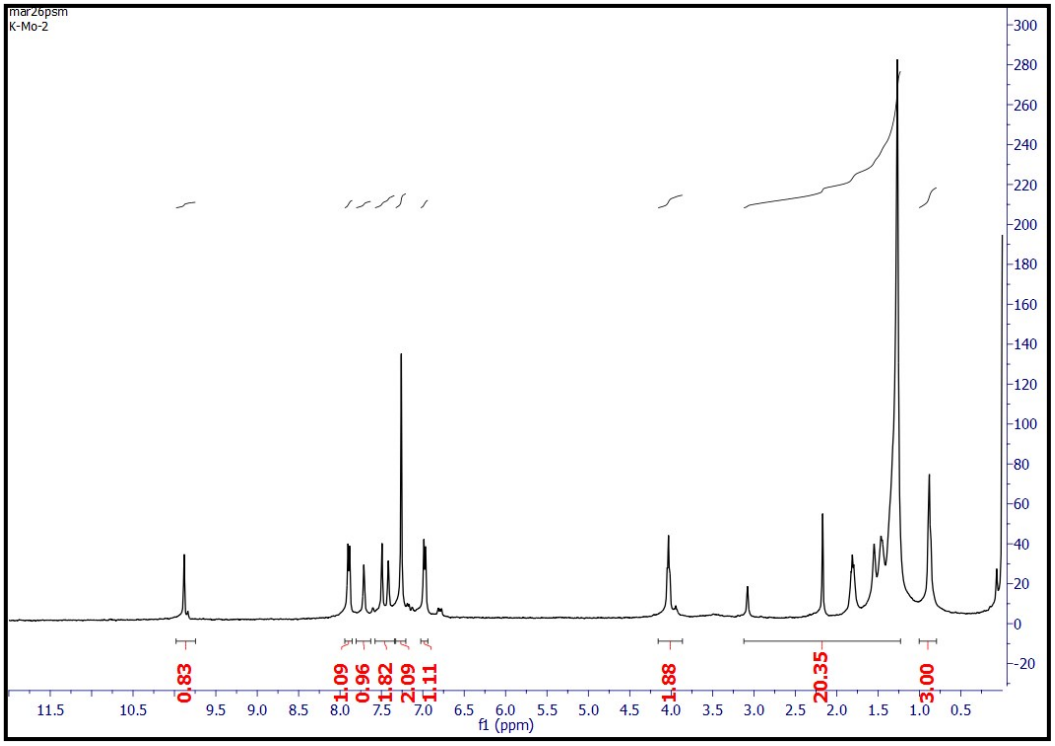


Figure S7. ^{1}H-NMR spectrum of intermediate **4a** recorded in DMSO-d_6

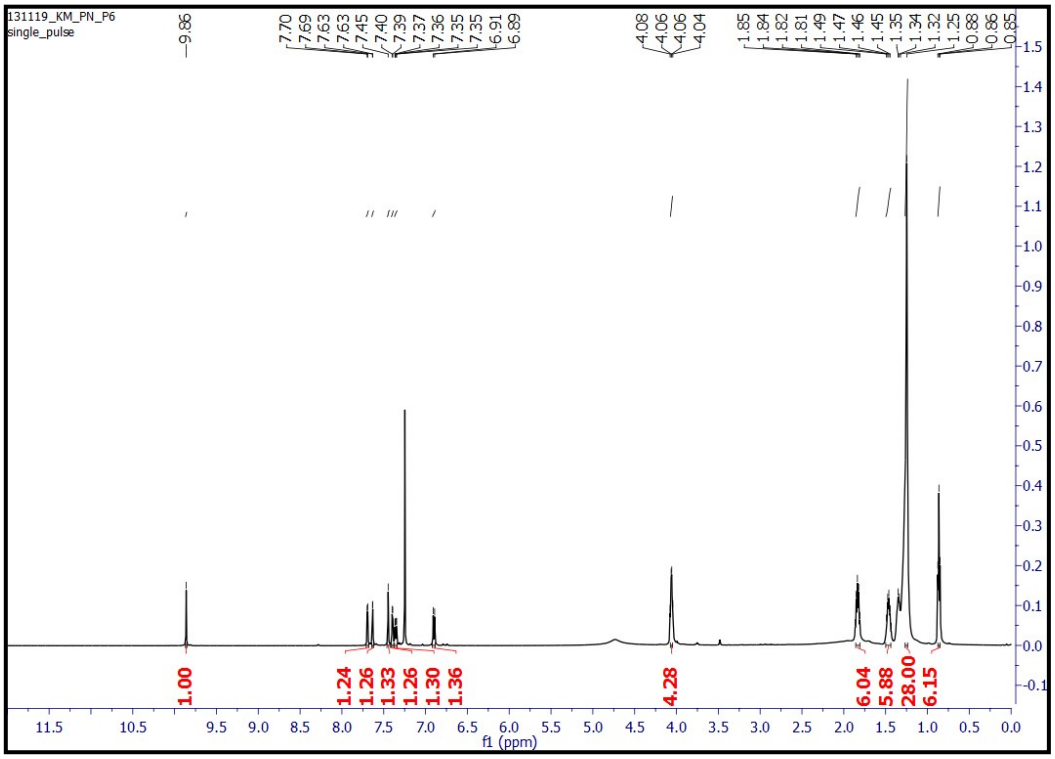


Figure S8. ^{1}H-NMR spectrum of intermediate **4b** recorded in DMSO-d_6

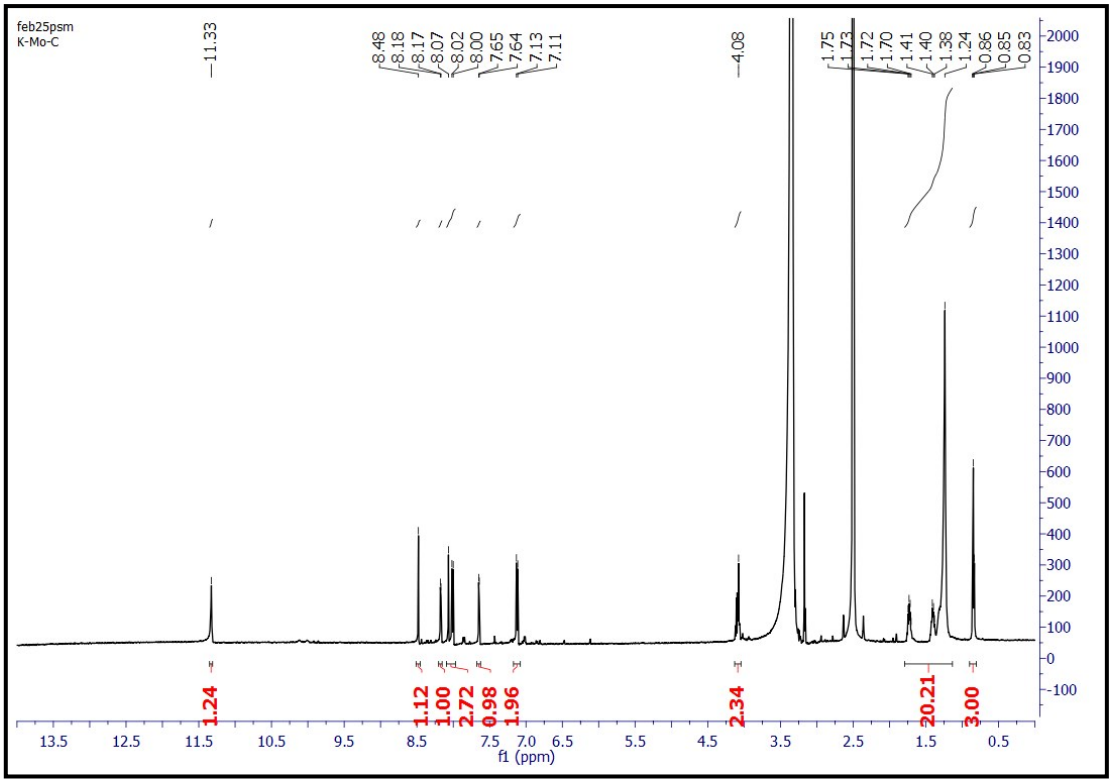


Figure S9. ^{1}H-NMR spectrum of $\mathbf{T_1}$ recorded in DMSO-d_6

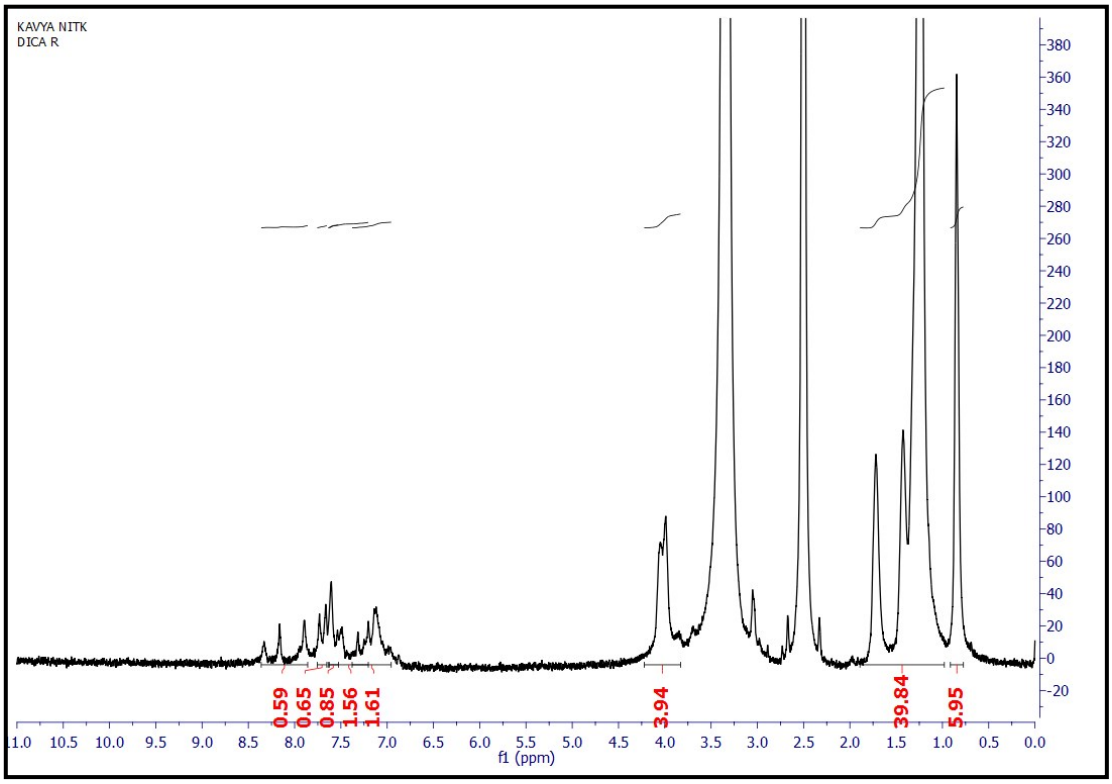


Figure S10. ^{1}H-NMR spectrum of $\mathbf{T_2}$ recorded in DMSO-d_6

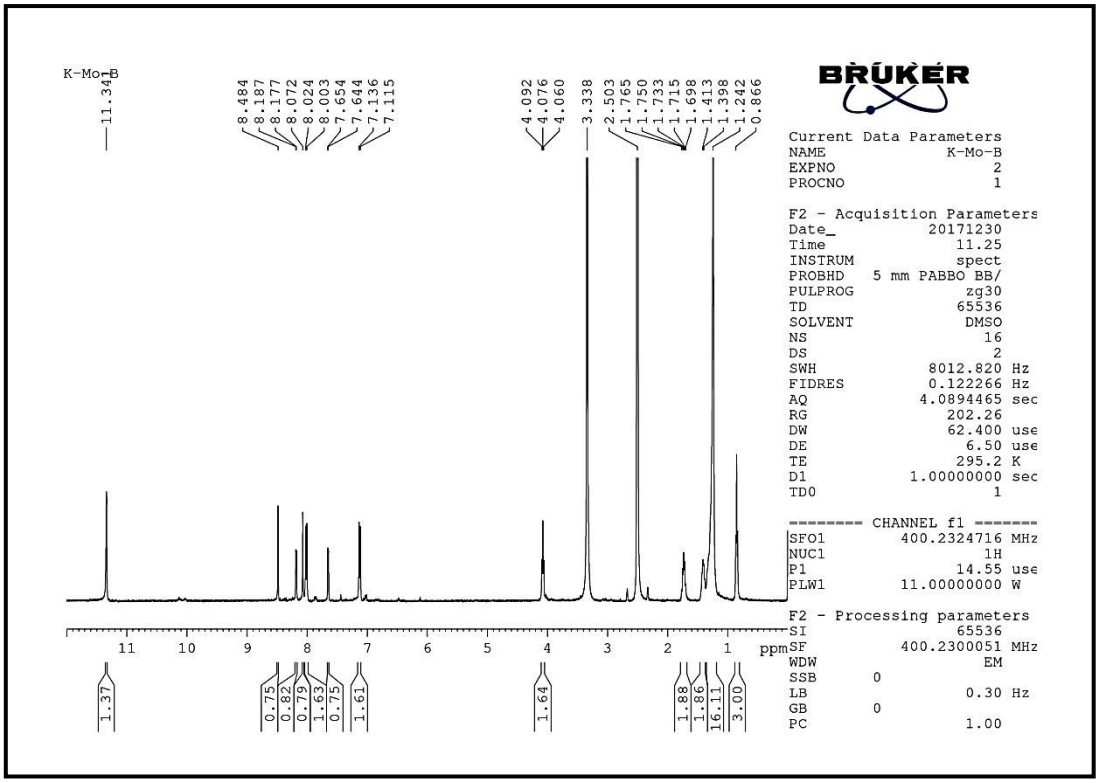


Figure S11. ^{1}H-NMR spectrum of $\mathbf{T_3}$ recorded in DMSO-d_6

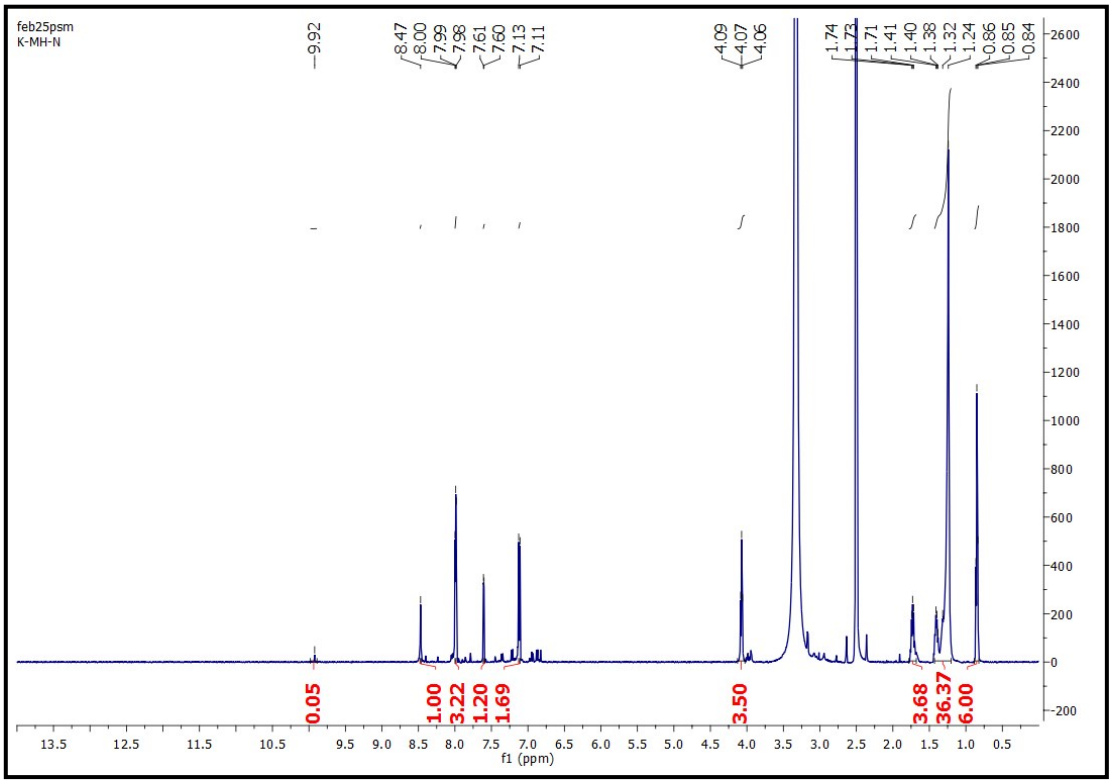


Figure S12. ^{1}H-NMR spectrum of $\mathbf{T_4}$ recorded in DMSO-d_6

Mass spectra

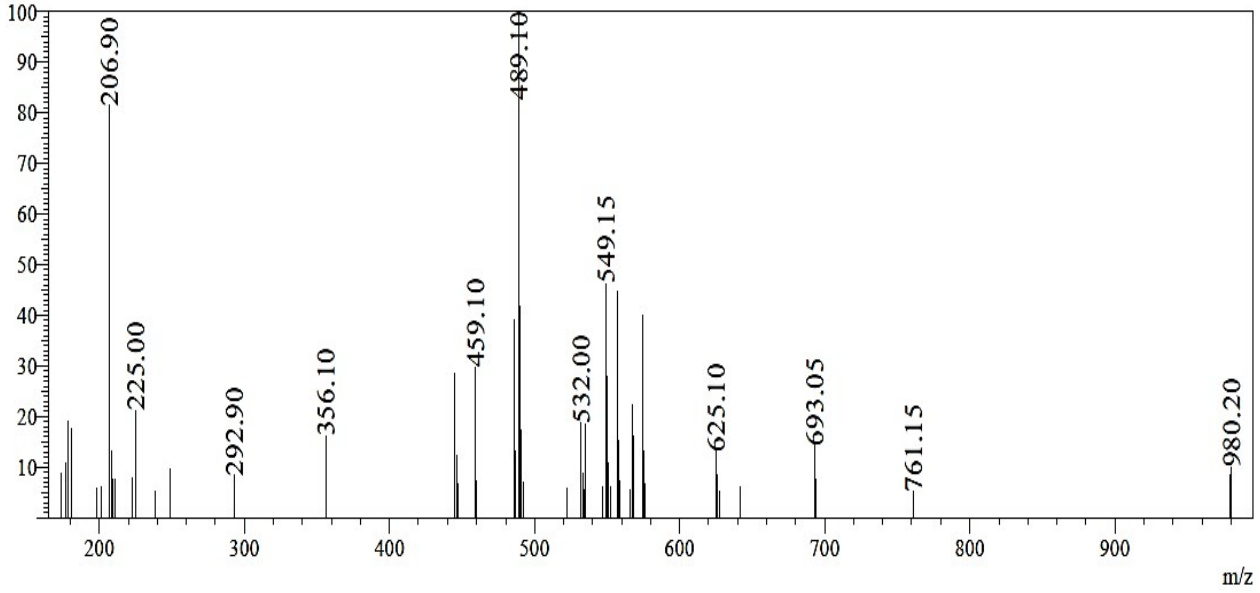


Figure S13. LCMS spectrum of $\mathbf{T_1}$

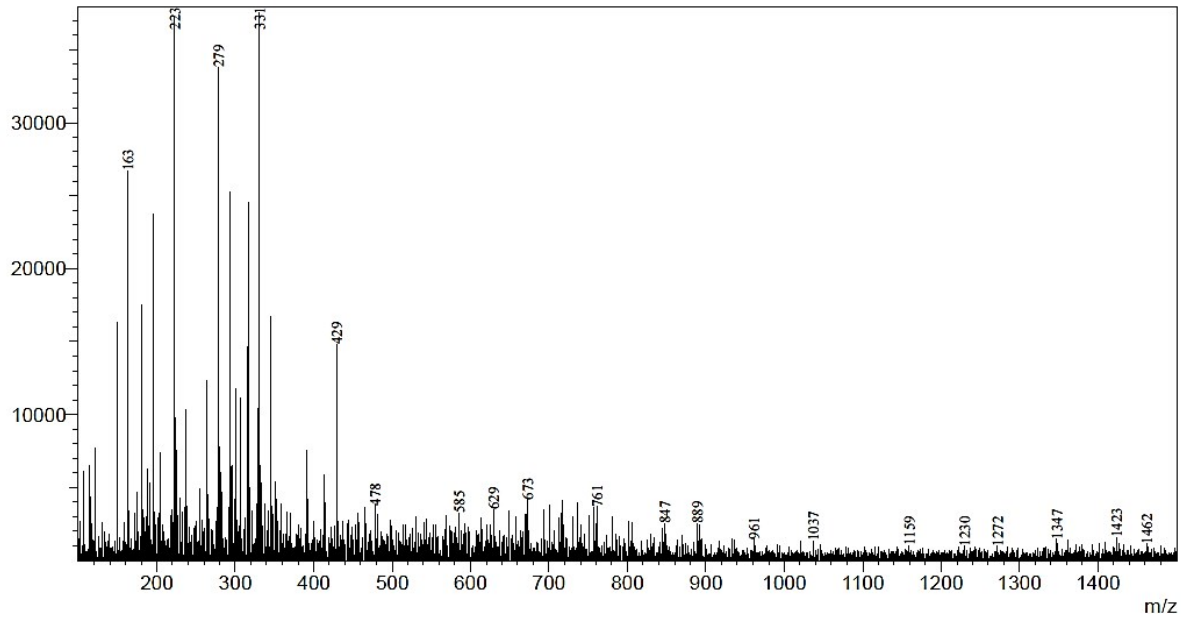


Figure S14. LCMS spectrum of $\mathbf{T_2}$

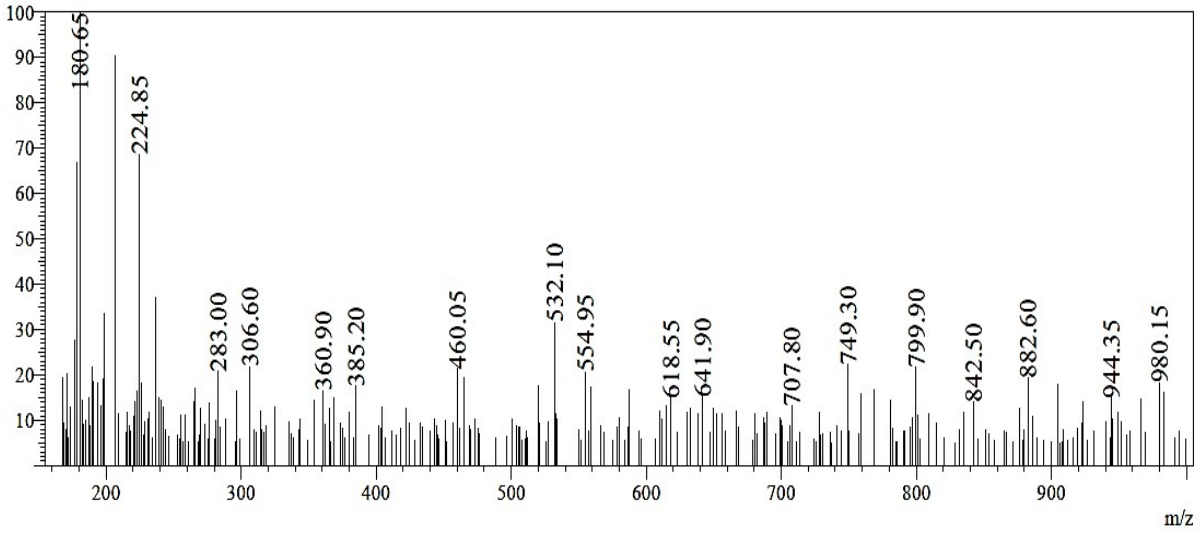


Figure S15. LCMS spectrum of $\mathbf{T_3}$

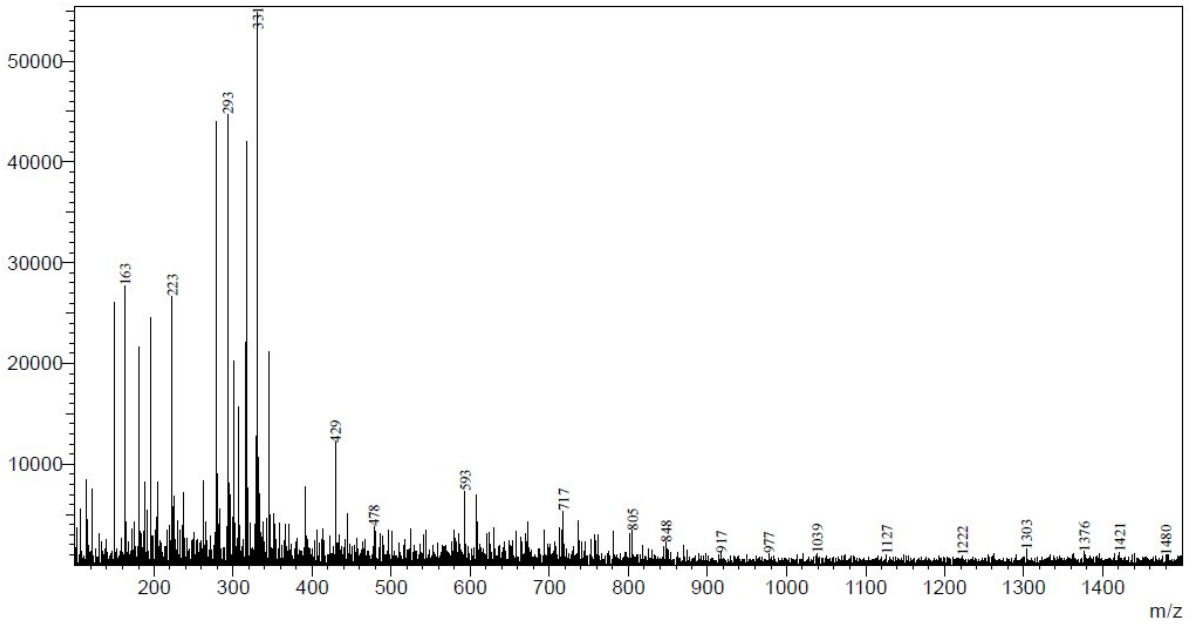


Figure S16. LCMS spectrum of $\mathbf{T_4}$

4. HOMO, LUMO, and optimized geometries of dyes T_{1-4}

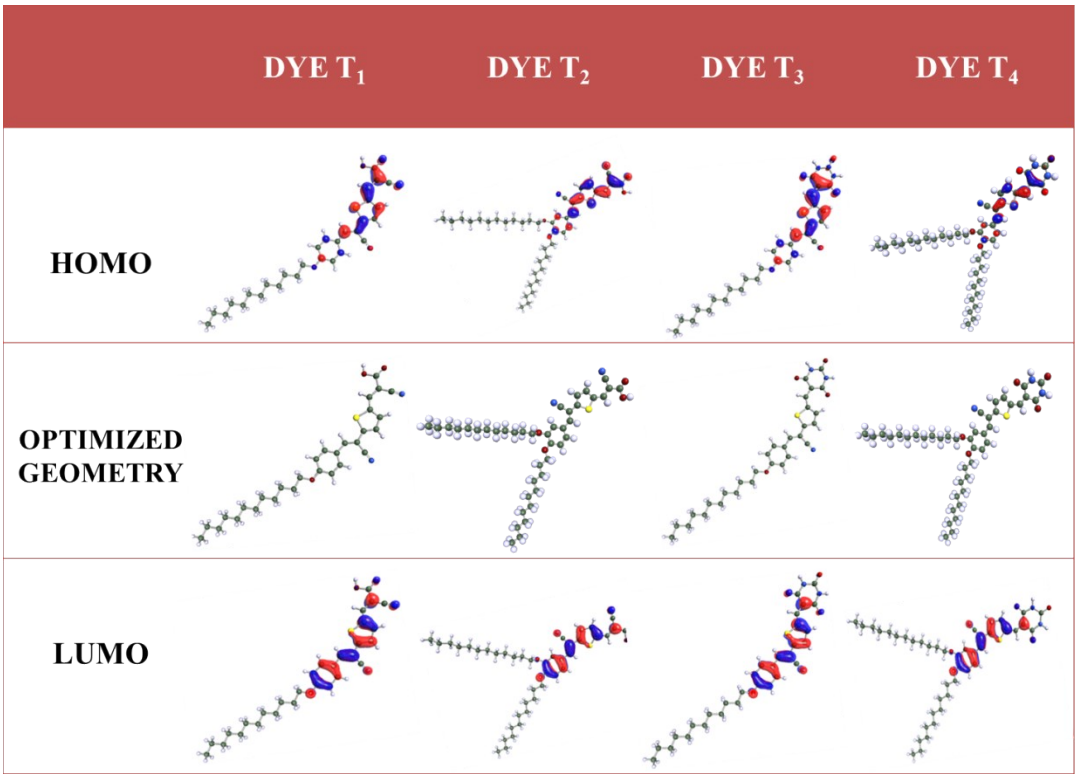
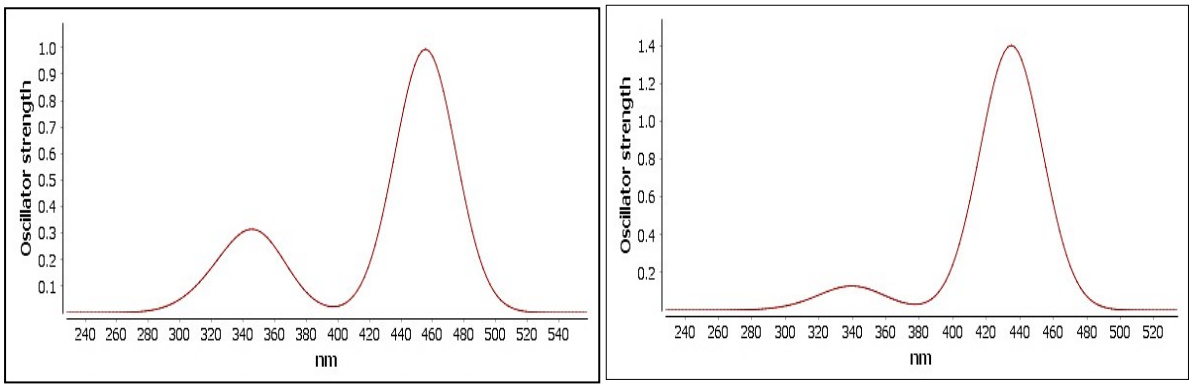


Figure S17. Optimized geometries and frontier molecular orbitals (HOMO and LUMO) of dyes $\mathbf{T_{1-4}}$

5. Theoretical UV-visible spectra of T_{1-4}



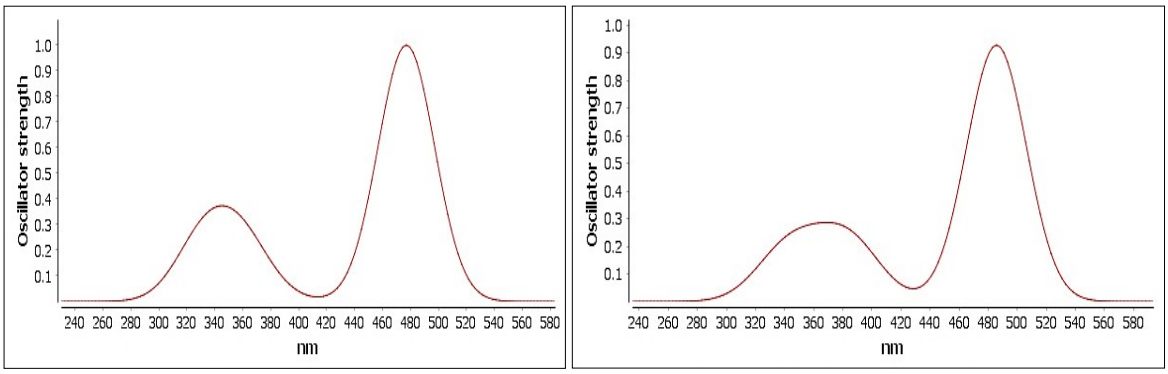


Figure S18. Simulated electronic excitation spectra of $\mathbf{T_{1\text{-}4}}$

6. Theoretical FTIR spectra of $T_{1\text{-}4}$

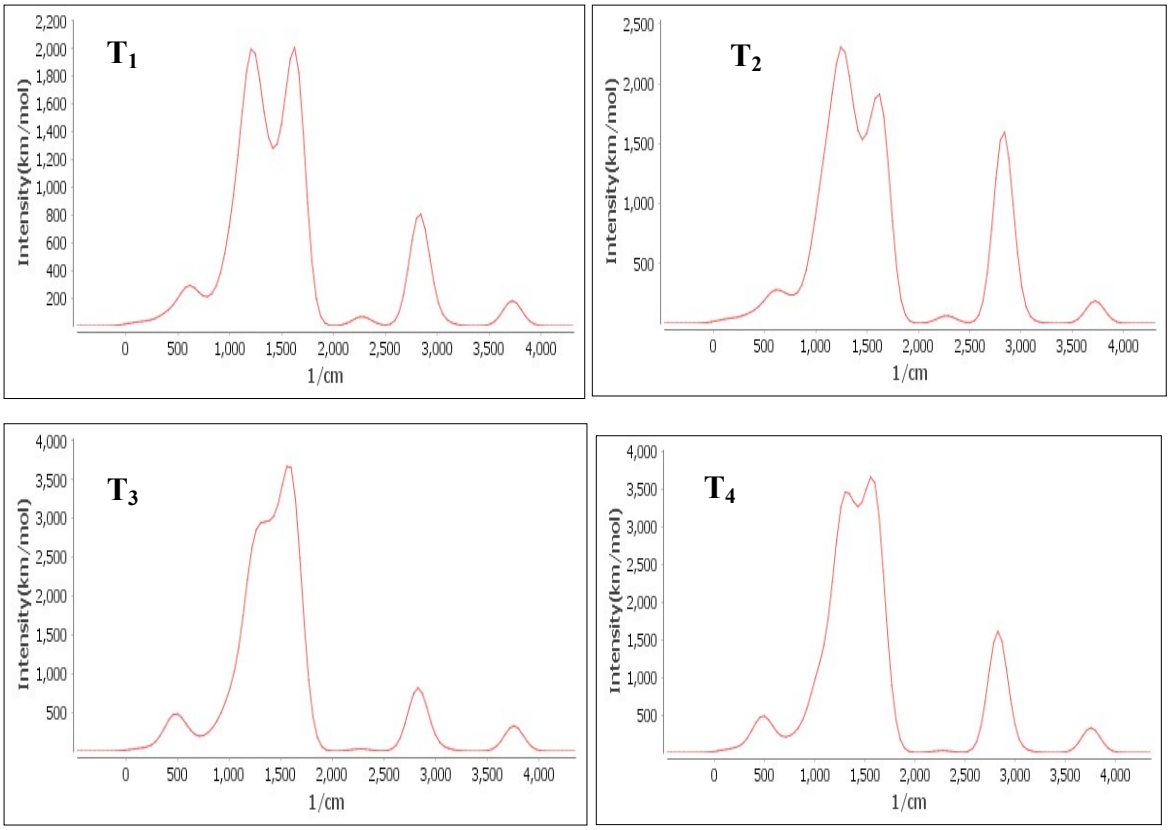


Figure S19. Theoretically obtained FT-IR spectra of $\mathbf{T_{1\text{-}4}}$

7. DOS plots of T_{1-4}

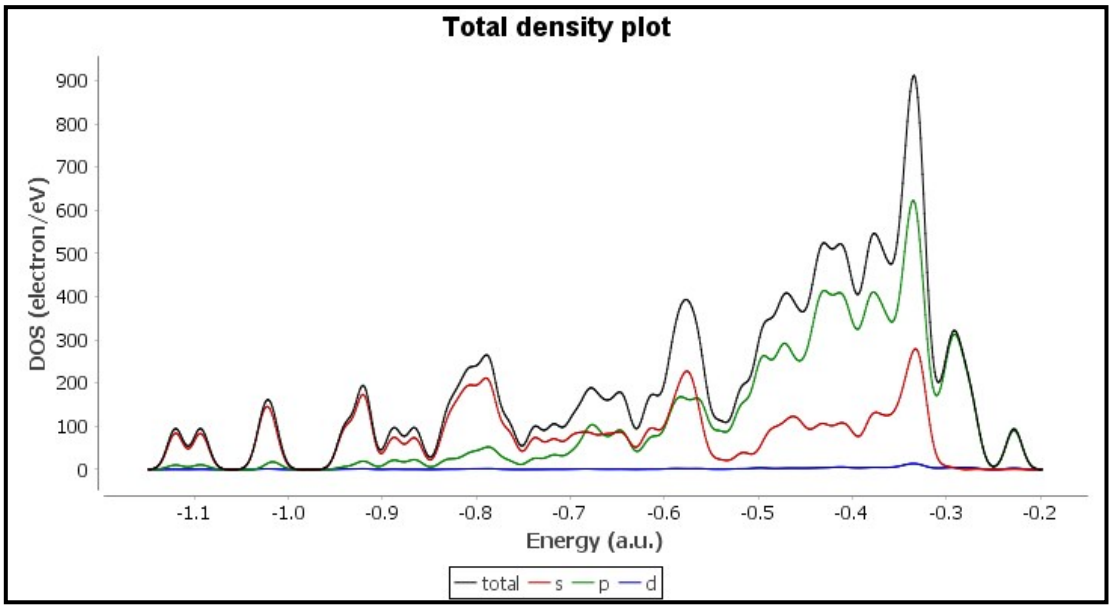


Figure S20. DOS plot of T_1

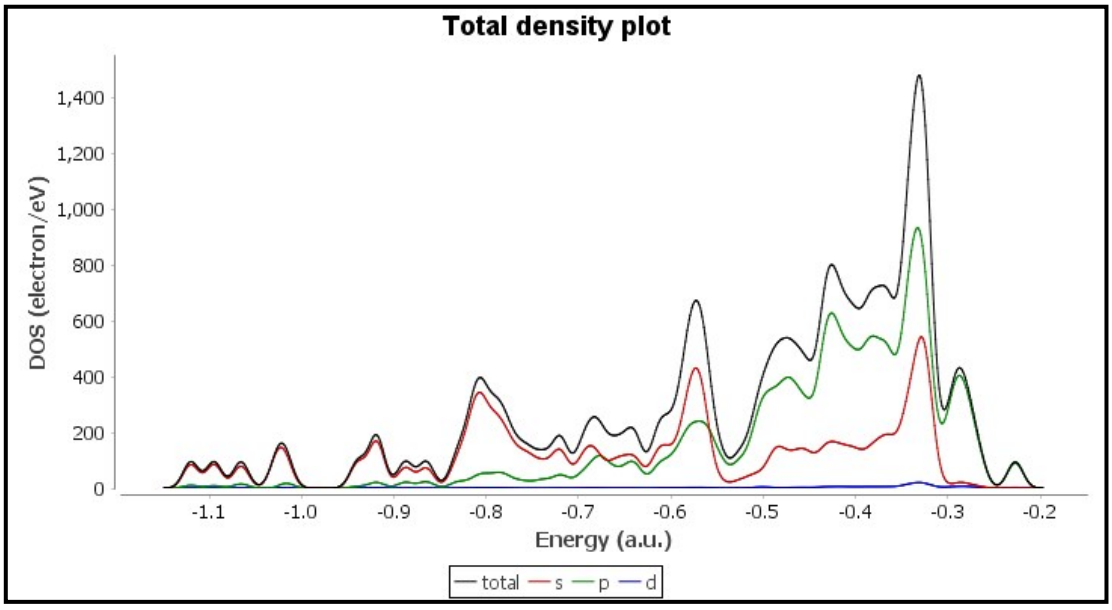


Figure S21. DOS plot of T_2

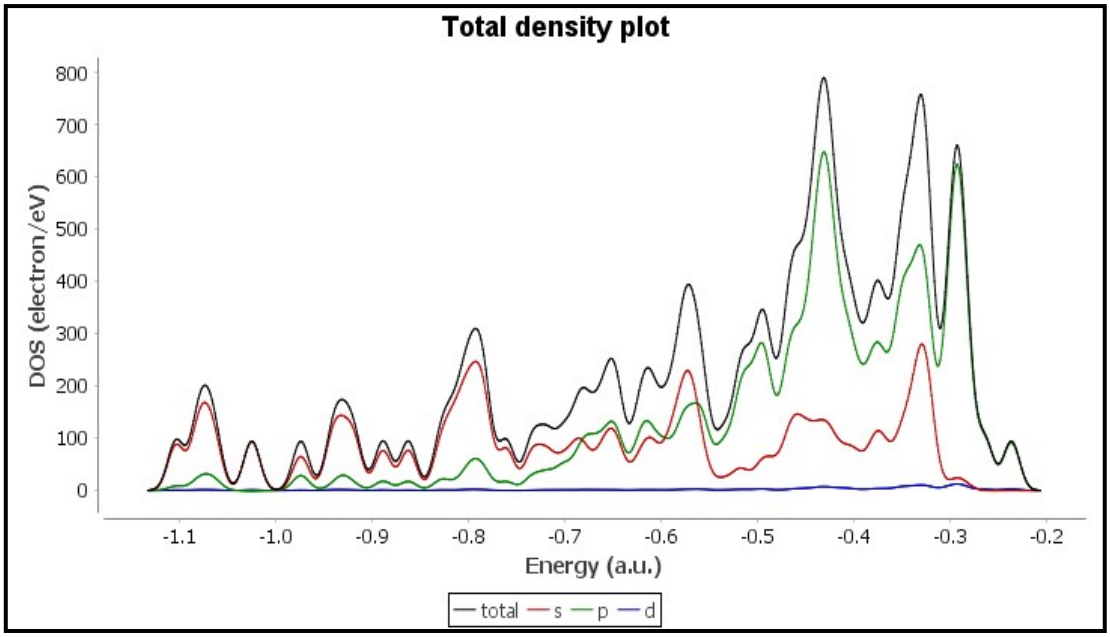


Figure S22. DOS plot of $\mathbf{T_3}$

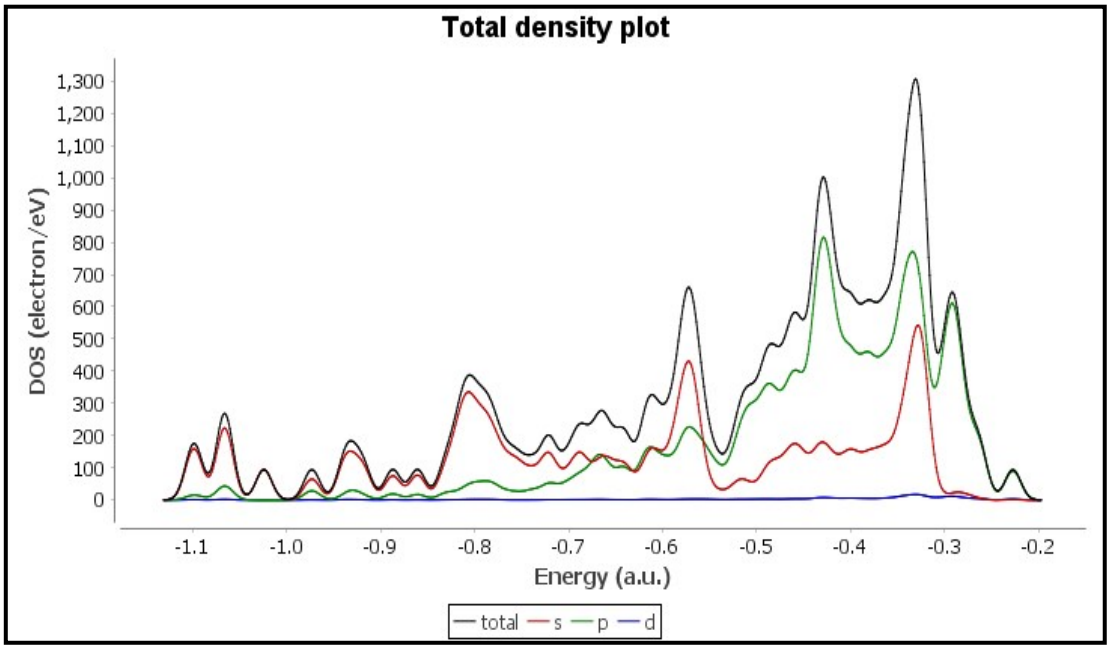


Figure S23. DOS plot of $\mathbf{T_4}$

8. UV-vis absorption spectra of T_{1-4} in acidic and basic mediums

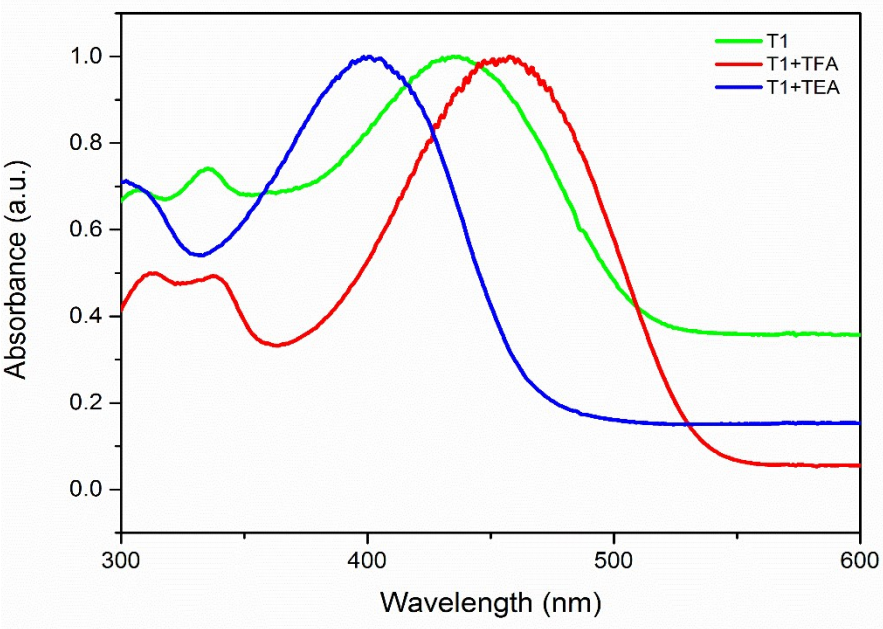


Figure S24. UV-vis absorption spectra of T_1 in acidic and basic mediums

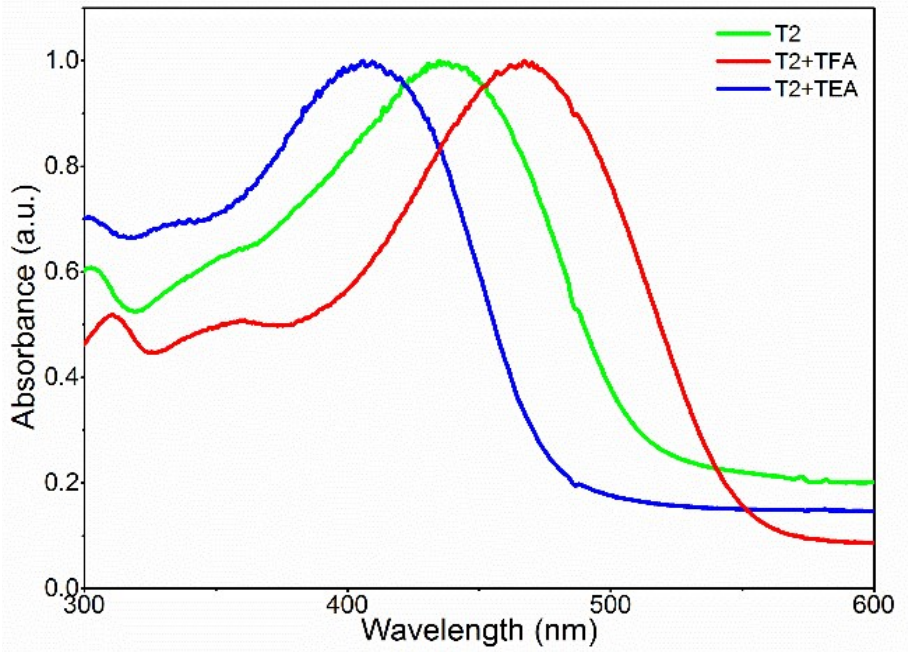


Figure S25. UV-vis absorption spectra of T_2 in acidic and basic mediums

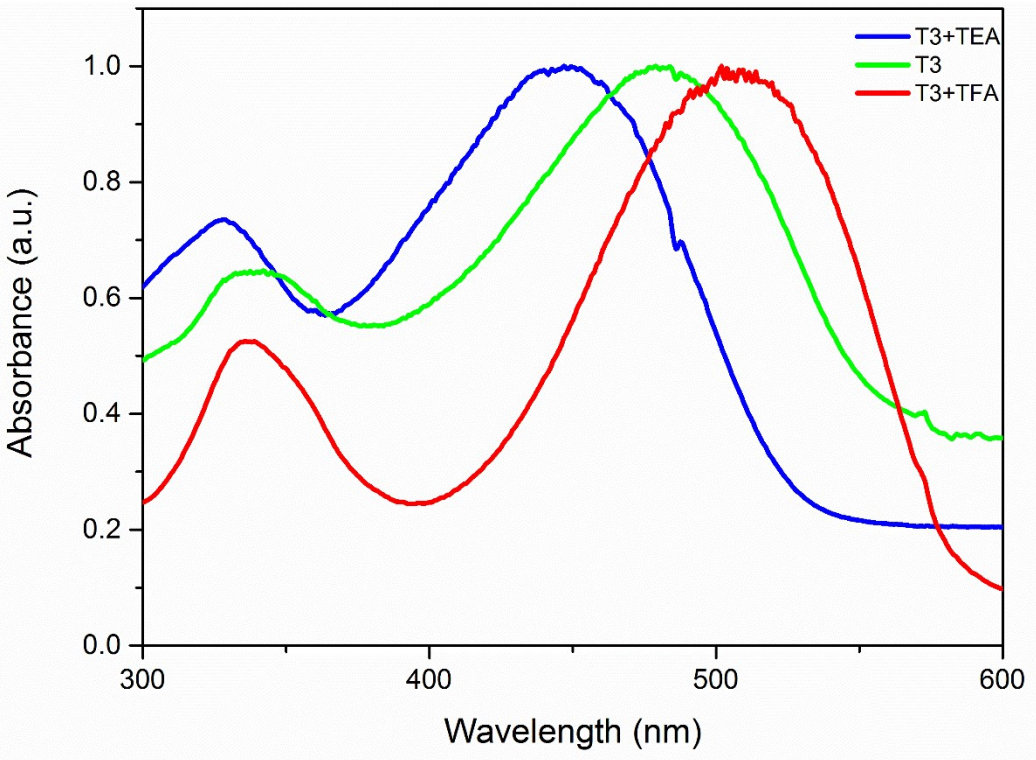


Figure S26. UV-vis absorption spectra of $\mathbf{T_3}$ in acidic and basic mediums

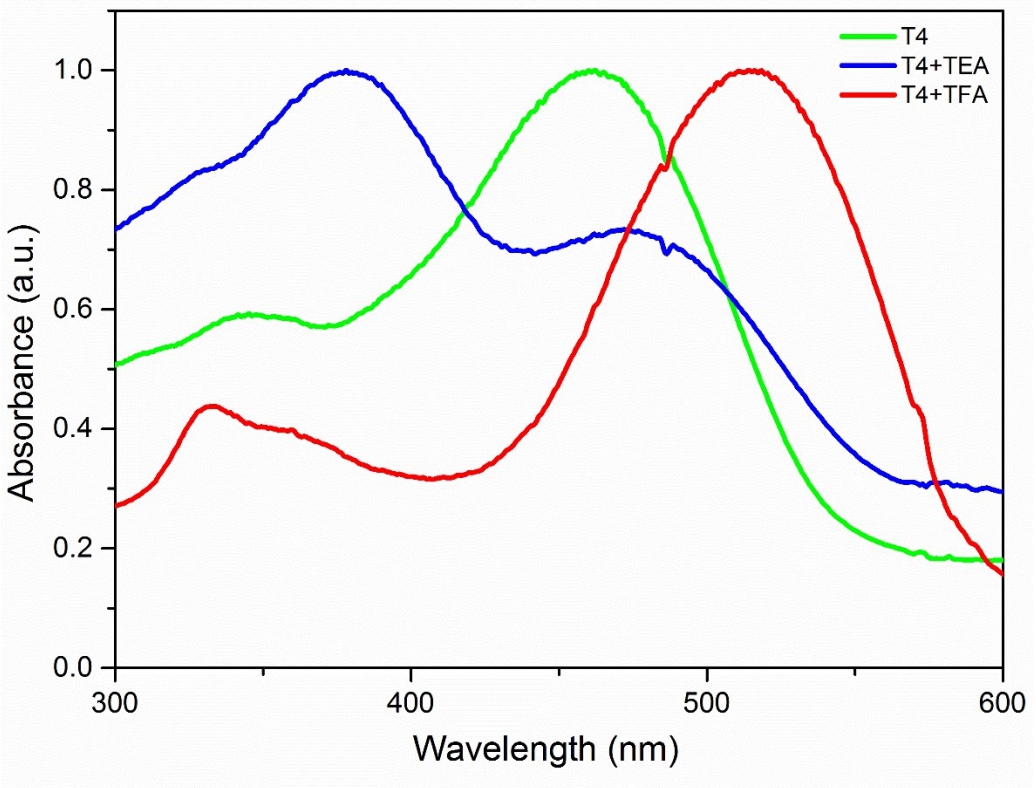


Figure S27. UV-vis absorption spectra of $\mathbf{T_4}$ in acidic and basic mediums

9. Normalized fluorescence emission spectra of T_{1-4} in acidic and basic mediums

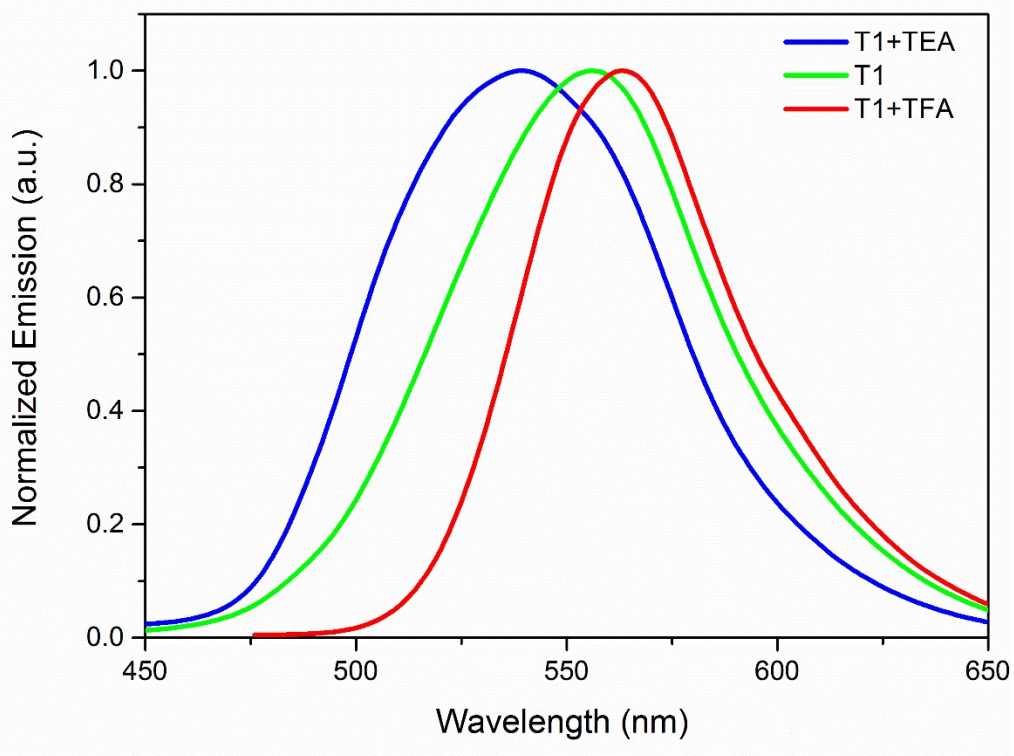


Figure S28. Normalized fluorescence emission spectra of T_1 in acidic and basic mediums

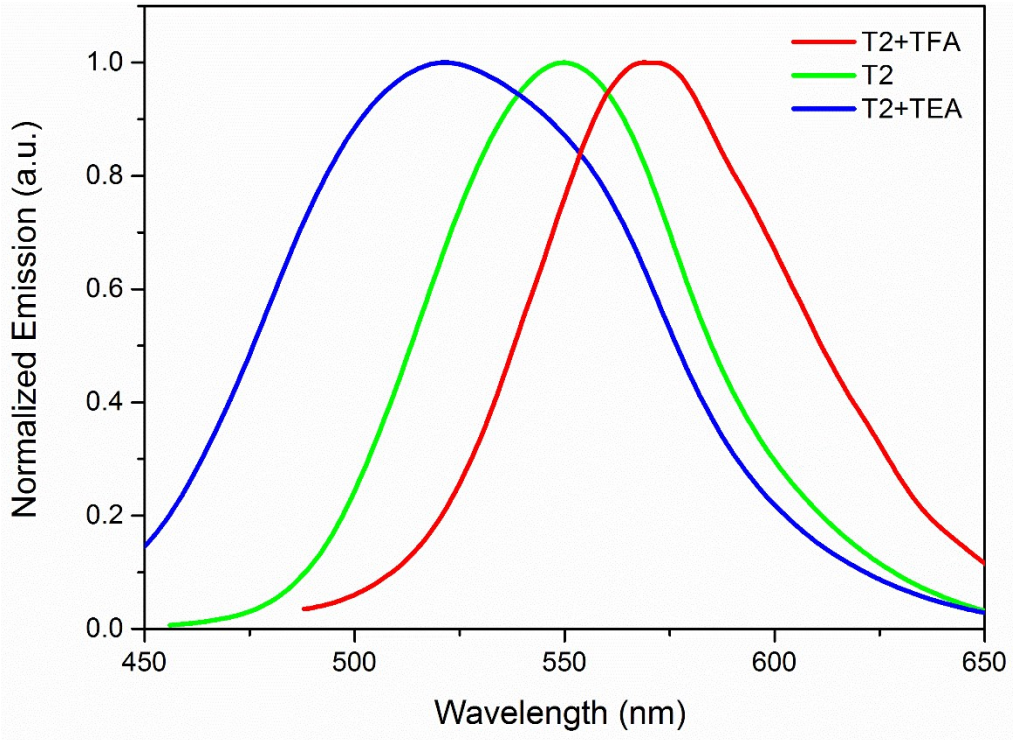


Figure S29. Normalized fluorescence emission spectra of T_2 in acidic and basic mediums

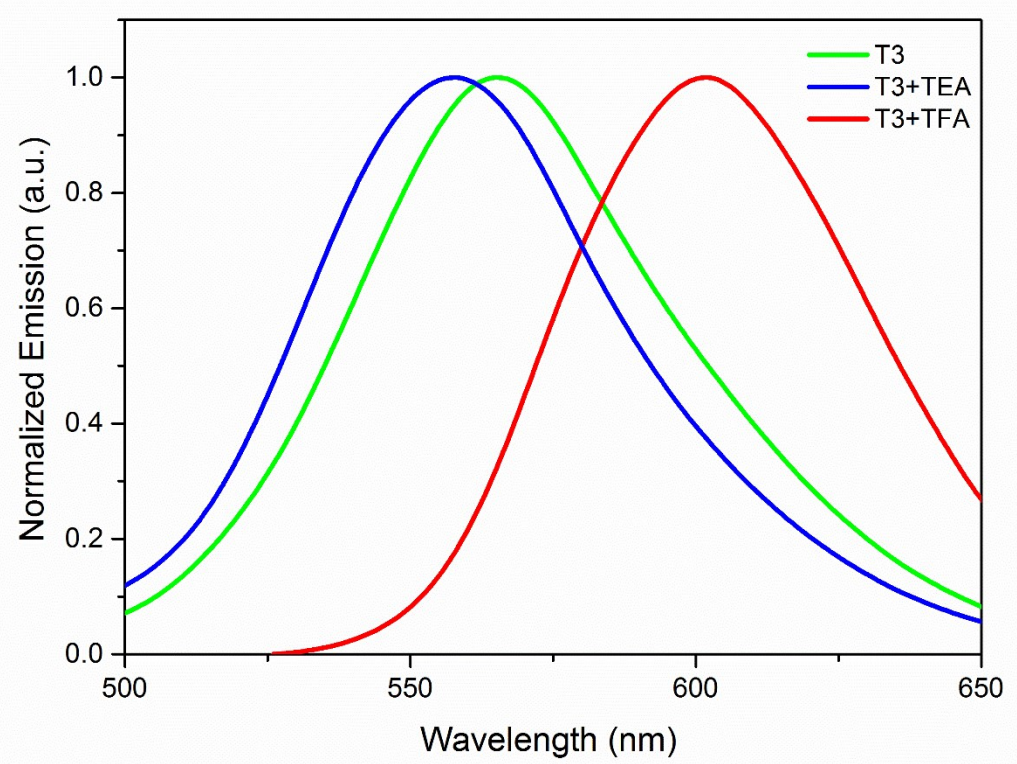


Figure S30. Normalized fluorescence emission spectra of $\mathbf{T_3}$ in acidic and basic mediums

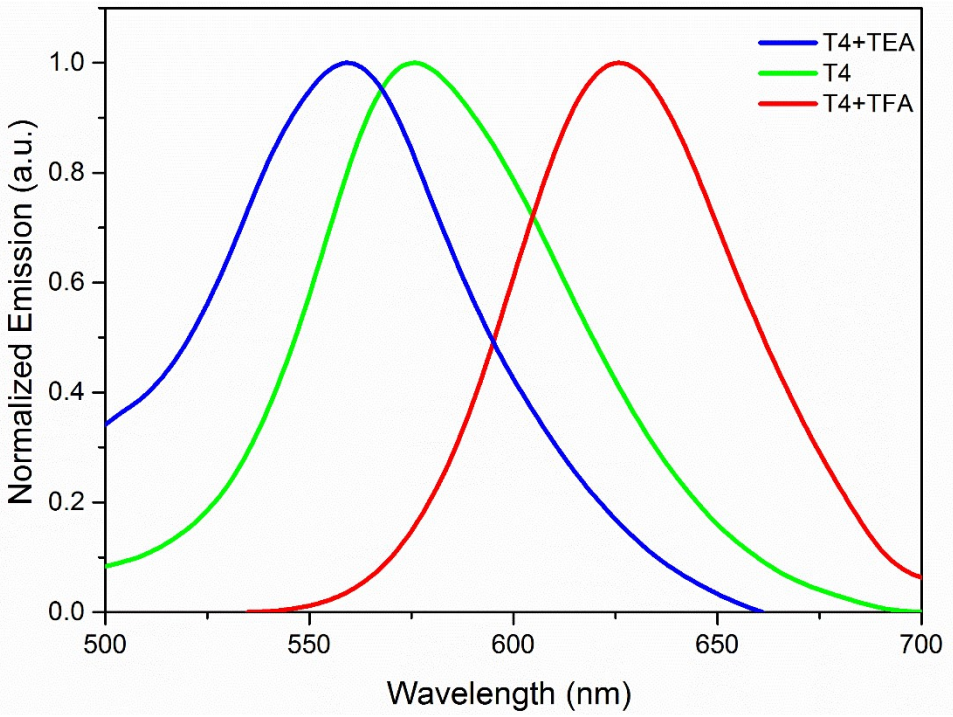


Figure S31. Normalized fluorescence emission spectra of $\mathbf{T_4}$ in acidic and basic mediums

10. DSC profile of dye T_2

The melting temperature (T_m) of **T_2** was found to be 297 °C, demonstrating the enhanced thermal stability of it.

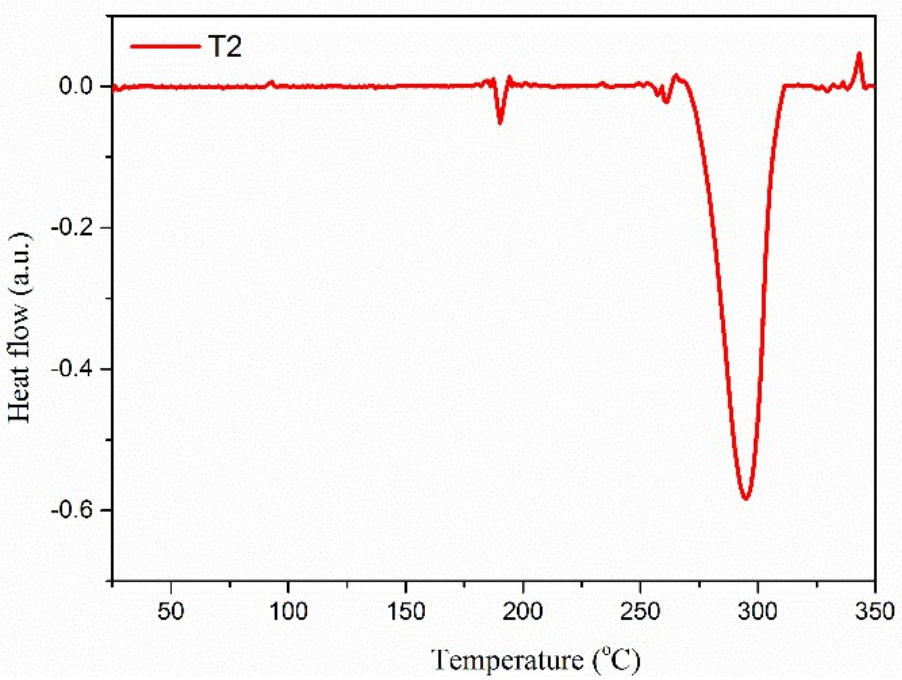


Figure S32. DSC profile of **T_2**

11. Cyclic voltammograms of T_{1-4}

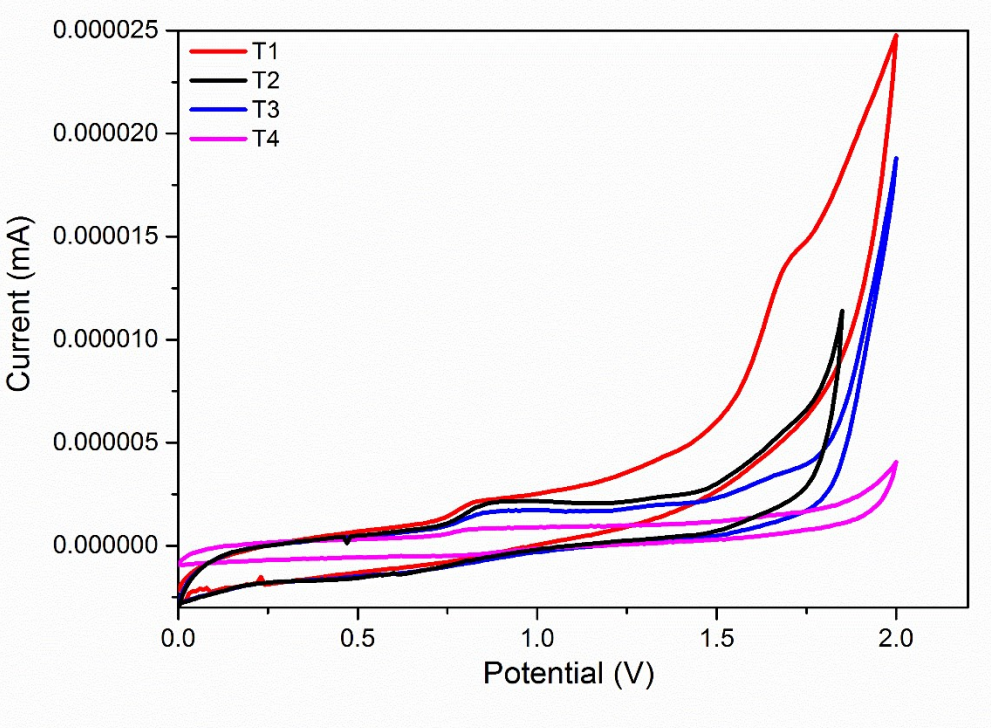


Figure S33. CV traces of dyes **T_{1-4}**

12. IPCE spectra and their integrated currents of dyes T_{1-4}

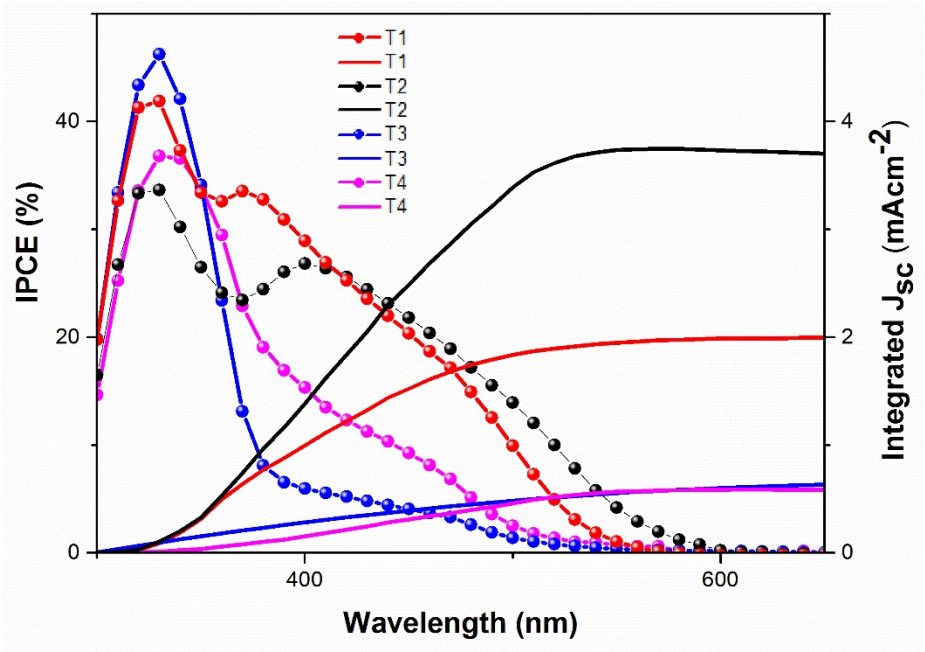


Figure S34. *IPCE* spectra and their integrated currents of DSSCs sensitized with dyes T_{1-4}.

13. IPCE spectra and their integrated currents of dyes MH-12 alone and co-sensitized using T_{1-4}

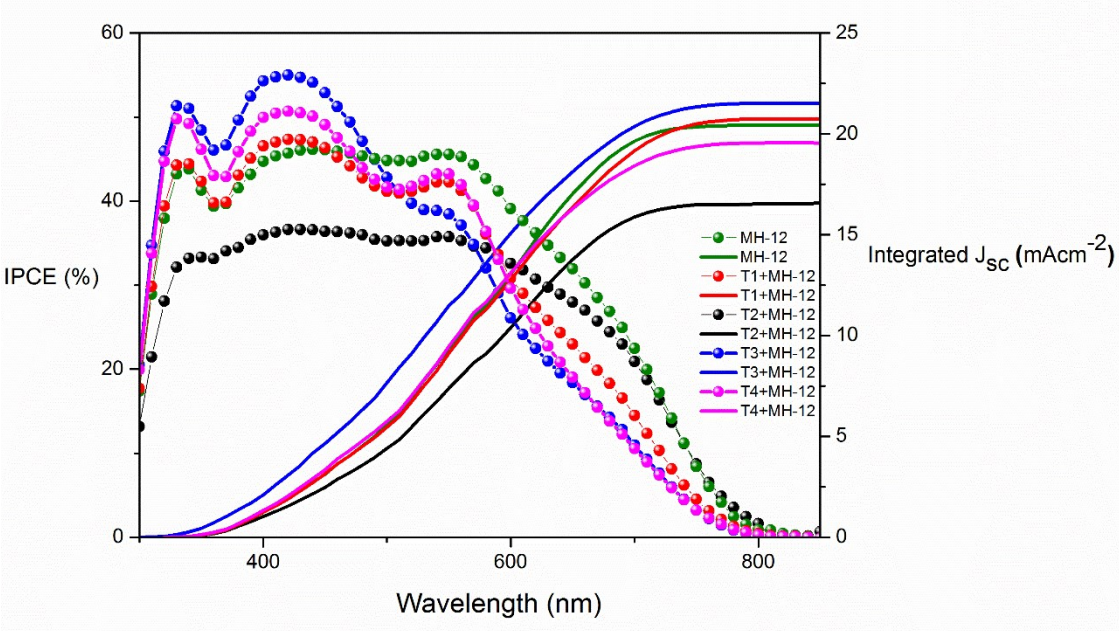


Figure S35. IPCE spectra of DSSCs sensitized with MH-12 alone and co-sensitized using T_{1-4}

14. EIS parameters and equivalent circuit

Sensitizer/ co-sensitizer	R_S (Ω)	R_{CT} (Ω)	R_{Pt} (Ω)
T_1	18.92	19.82	77.27
T_2	18.98	28.47	168.52
T_3	18.56	296.8	355.9
T_4	18.96	356.3	19.574
MH-12	22.05	13.79	12.67
T_1 + MH-12	20.32	15.31	4.09
T_2 + MH-12	19.46	16.82	4.78
T_3+ MH-12	18.06	6.33	23.18
T_4 + MH-12	19.82	18.48	6.67

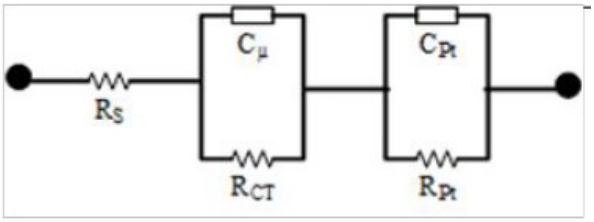


Table S1. EIS parameters and equivalent circuit used for devices sensitized and co-sensitized with dyes **T_{1-4}**

15. FTIR spectra of T_{1-4} adsorbed on TiO_2 surface

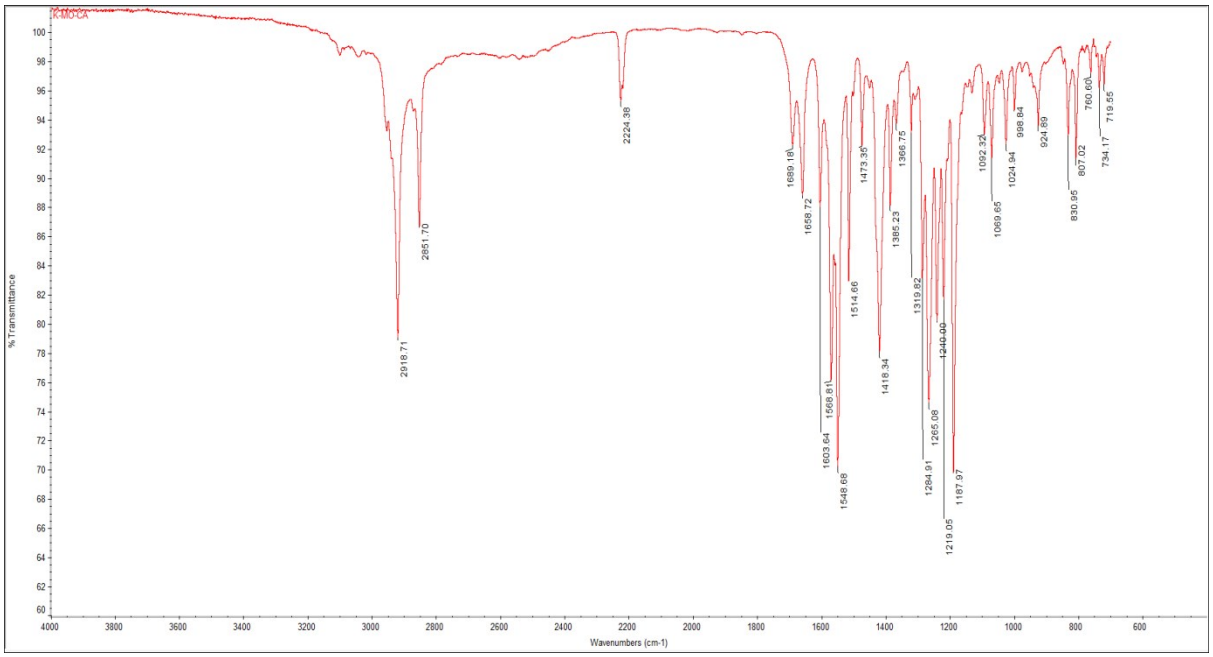


Figure S36. FTIR spectrum of $\mathbf{T_1}$ adsorbed on TiO_2 surface

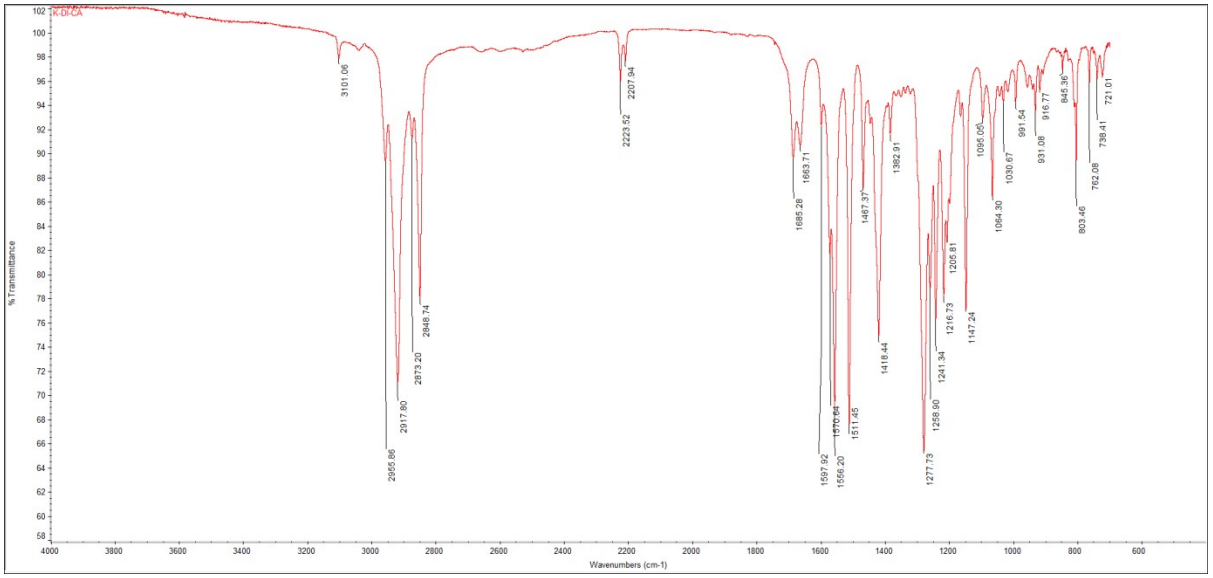


Figure S37. FTIR spectrum of $\mathbf{T_2}$ adsorbed on TiO_2 surface

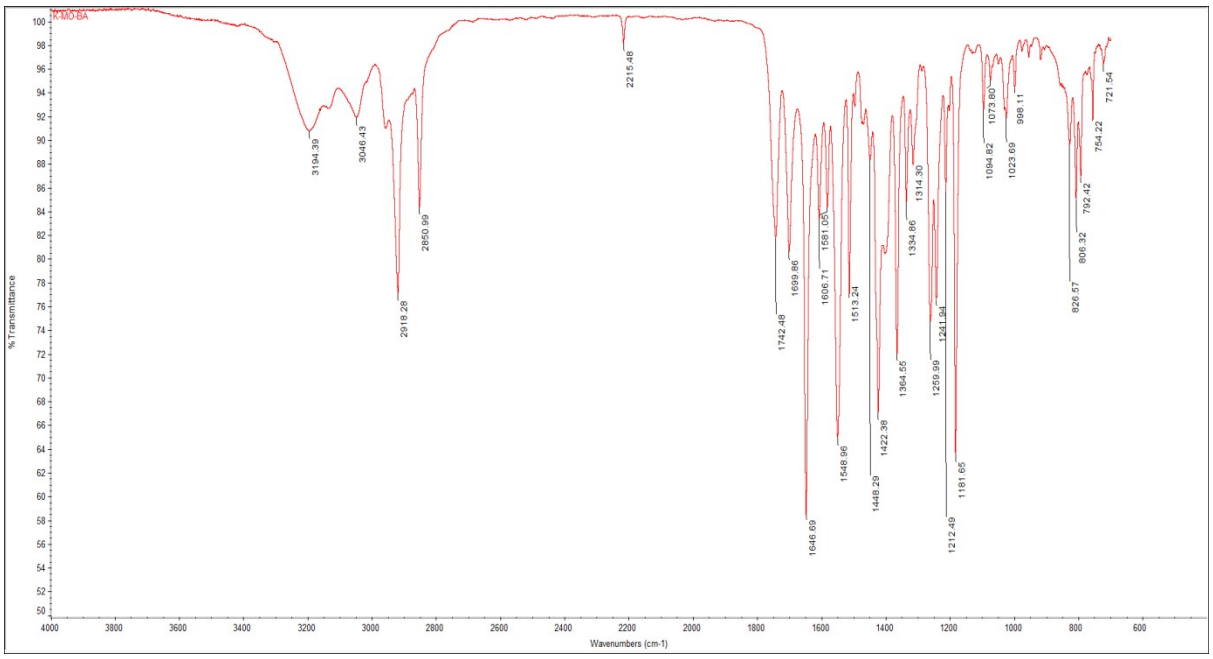


Figure S38. FTIR spectrum of $\mathbf{T_3}$ adsorbed on TiO_2 surface

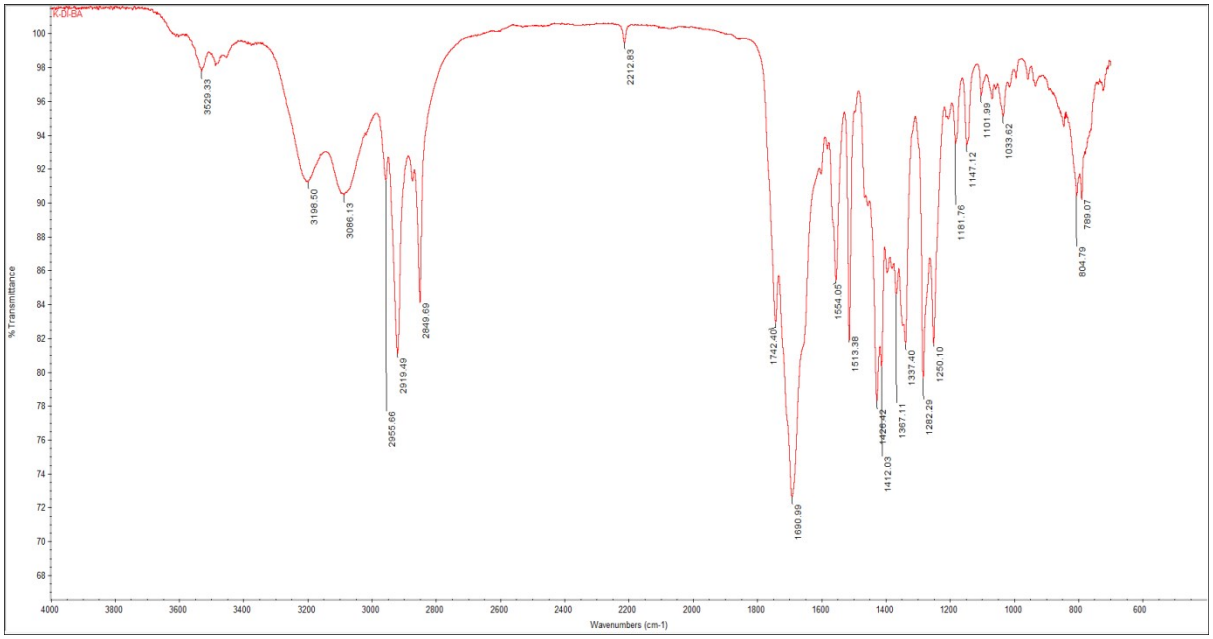


Figure S39. FTIR spectrum of $\mathbf{T_4}$ adsorbed on TiO_2 surface

16. Device fabrication procedures

TiO_2 electrode preparation and device fabrication using new dyes as sensitizers

Fluorine-doped tin oxide (FTO) coated glasses (thickness 2.2 mm, sheet resistance 8 Ω/cm^2, TEC, Pilkington) were washed gently with soap solution, distilled water, acetone, and ethanol, *respectively*. After that, washed FTO glasses were immersed in 40 mM aqueous $TiCl_4$ solution (Wako pure chemical industries, Ltd.) at 70 °C for half an hour and further, once it is cooled, rinsed with water and ethanol. A thin layer of (thickness around 8-10 μm) of TiO_2 paste (Solaronix, Ti-Nanoxide D/SP) was coated on transparent substrates (active area 0.18 cm^2) by screen-printer followed by drying at 350 °C for 10 min and annealing at 500 °C for half an hour, which serves as a seed layer. Further, after drying the electrodes, scattering layer (5 μm thick) TiO_2 particles were reprinted onto the already deposited TiO_2 layer and annealed at 350 °C for 10 min followed by 500 °C for half an hour. After attaining room temperature, TiO_2 electrodes were treated with 40 mM aqueous $TiCl_4$ solution at 70 °C for half an hour followed by rinsing with water and ethanol, which fills the defective "pin-holes" present in the TiO_2 layer. Later, before dipping into the dye solution, the electrodes were annealed again at 500 °C for 30 minutes and left to cool to 80 °C. The required dye solutions (0.2 mM) were prepared in 10 mL by dissolving $\mathbf{T_{1\text{-}4}}$ in a mixture of 1:1:1 acetonitrile, *tert*-butanol, and dimethyl sulfoxide (DMSO) solvents. Chenodeoxycholic acid (CDCA) was added to a concentration of 20 mM. The hot electrodes were immersed in dye solutions and kept at room temperature for 20 hours for better adsorption onto the TiO_2 surface.

To prepare the counter electrode, pre-cut transparent conductive oxide (TCO) glasses were washed with distilled water followed by 0.1 M HCl solution in ethanol, followed by sonication in an acetone bath for 15 minutes. The cleaned TCO were then dried at 400 °C for 15 minutes. A thin layer of Pt-paste (Solaronix, Plastisol T/SP) on TCO was printed uniformly and then electrodes were annealed at 450 °C for 10 minutes. The dye-sensitized TiO_2 electrodes were sandwiched with Pt counter electrodes and liquid electrolyte (Solaronix, Iodolyte HI-30) was then injected into the cell, while the two electrodes were held together with the clips.

TiO_2 electrode preparation and device fabrication using new dyes T_{1-4} as co-sensitizers

Fluorine-doped tin oxide (FTO) coated glasses (thickness 2.2 mm, sheet resistance 8 Ω/cm^2, TEC, Pilkington) were washed gently with soap solution, distilled water, acetone, and ethanol, respectively. After that, washed FTO glasses were immersed in 40 mM aqueous $TiCl_4$ solution (Wako pure chemical industries, Ltd.) at 70 °C for half an hour and further, once it was cooled, rinsed with water and ethanol. A thin layer of (thickness around 8-10 μm) of TiO_2 paste (Solaronix, Ti-Nanoxide D/SP) was coated on transparent substrates (active area 0.18 cm^2) by screen-printer followed by drying at 350 °C for 10 min and annealing at 500 °C for half an hour, which serves as a seed layer. Further, after drying the electrodes, scattering layer (5 μm thick) TiO_2 particles were reprinted onto the already deposited TiO_2 layer and annealed at 350 °C for 10 min followed by 500 °C for half an hour. After attaining room temperature, TiO_2 electrodes were treated with 40 mM aqueous $TiCl_4$ solution at 70 °C for half an hour followed by rinsing with water and ethanol, which fills the defective "pin-holes" present in the TiO_2 layer. Later, before dipping into the dye solution, the electrodes were annealed again at 500 °C for 30 minutes and left to cool to 80 °C. The dye solutions were prepared in 10 mL by dissolving **MH-12** (0.2 mM) and **T_{1-4}** (0.2 mM) dyes in a mixture of 1:1:1 acetonitrile, *tert*-butanol, and dimethyl sulfoxide (DMSO) solvents. Chenodeoxycholic acid (CDCA) was added at the concentration of 20 mM. The hot electrodes were immersed in dye solutions and kept at room temperature for 20 hours for better adsorption onto the TiO_2 surface.

To prepare the counter electrode, pre-cut TCO glasses were washed with distilled water followed by 0.1 M HCl solution in ethanol, followed by sonication in an acetone bath for 15 minutes. The cleaned TCO were then dried at 400 °C for 15 minutes. A thin layer of Pt-paste (Solaronix, Plastisol T/SP) on TCO was printed uniformly and then electrodes were annealed at 450 °C for 10 minutes. The dye-sensitized TiO_2 electrodes were sandwiched with Pt counter electrodes and liquid electrolyte (Solaronix, Iodolyte HI-30) was then injected into the cell, while the two electrodes were held together with the clips.

14. DFT calculations: Cartesian coordinates of T_{1-4}

14.1 Cartesian coordinates of T_1

ATOM	CARTESIAN COORDINATES		
1 c	-7.59986255721610	1.46210791068223	-0.23423737568115
2 c	-4.95417874604639	1.57832844851921	-0.09261938682685
3 c	-3.77954456150438	3.92505399009855	0.21067070505853
4 c	-5.24736672572614	6.08574127577898	0.35564392847117
5 c	-7.89902765090381	6.01765647370613	0.21082070421159
6 c	-9.03951117368847	3.62212340494506	-0.08695772972080
7 o	-3.72725765849558	-0.64724762428113	-0.26731133943697
8 c	-1.02438826980550	-0.70029331993795	-0.13017008551454
9 c	-0.17003418066326	-3.41928719425611	-0.42165719170086
10 c	2.70436370181618	-3.68566197421243	-0.25941850118750
11 c	3.61476992963183	-6.40699433042693	-0.60047235723769
12 c	6.48380154209601	-6.69399327572089	-0.40351218819234
13 c	7.40341889095816	-9.40732184974265	-0.77806513391280
14 c	10.27020892045805	-9.69934676006123	-0.55294798008209
15 c	11.19453341417787	-12.40763877912973	-0.95202299014273
16 c	14.05931535604203	-12.70327833823371	-0.70674187478562
17 c	14.98605445533634	-15.40852838217622	-1.11828420412631
18 c	17.84937625511064	-15.70813671858088	-0.86099709750915
19 c	18.75721803131297	-18.41614901687368	-1.28210399124175
20 c	-9.21002589469497	8.40305311928174	0.37264606732837

21 c	-11.70875418058442	9.03040948223240	0.28977857392357
22 c	-12.61047281176218	11.62769254190094	0.46872684606860
23 c	-15.09918776990411	12.43327997291294	0.39284714456194
24 c	-15.38953252826986	15.05587244874574	0.59681469565480
25 c	-13.12200670542307	16.34226634330710	0.83712439045593
26 s	-10.59843932117300	14.18912286670229	0.80532660749268
27 c	-12.52907061961875	18.95622097909460	1.08372329173844
28 h	-10.53862196592468	19.40012110026357	1.24618135100044
29 c	-14.09880568648280	21.00018962231530	1.14006476665182
30 h	-7.93909894069599	9.99705640961387	0.59343261892088
31 c	-13.11348743732700	23.60565551575013	1.40125771820128
32 o	-14.41243099972908	25.47459949362274	1.44930499322229
33 o	-10.55532974591380	23.70174005534144	1.58411106091252
34 c	-13.66335773530791	7.18717528596318	0.01056803230569
35 n	-15.29693597788740	5.76097295021177	-0.21238738067580
36 c	-16.77365985211263	20.79507444288506	0.94742757183985
37 n	-18.93288750604993	20.54664418414487	0.78548855344198
38 h	-8.48153050581265	-0.36691799453082	-0.46511431415416
39 h	-1.74979194666320	4.08045948718361	0.33116909158604
40 h	-4.31386418442101	7.89251475386448	0.58721018031800
41 h	-11.06662197540740	3.44826581762761	-0.20535041705193
42 h	-0.23595026928609	0.48208318689052	-1.63374275675138
43 h	-0.41485907222652	0.07355008618291	1.68911413494764

44 h	-1.07119812445244	-4.56091571721538	1.04492192678529
45 h	-0.84790470711648	-4.13816939204378	-2.23534126380672
46 h	3.59312309155971	-2.48906274484191	-1.69605039537081
47 h	3.36124064688714	-2.97295613929071	1.56928599245613
48 h	2.70734933940981	-7.61167680488303	0.81687859034766
49 h	2.97992153436989	-7.11023928860793	-2.44024297382100
50 h	7.39105902902874	-5.46804181698519	-1.80379026560350
51 h	7.11209079261058	-6.01005472892229	1.44657193714775
52 h	6.48124733789105	-10.63773162334832	0.60823088304537
53 h	6.79166034411169	-10.08303915371710	-2.63656531053840
54 h	11.19330674752798	-8.45513477393607	-1.92658769492716
55 h	10.87811119910494	-9.03935662526849	1.31262664710127
56 h	10.26096224612368	-13.65464001159132	0.41182428664955
57 h	10.59852159013818	-13.06188239510201	-2.82338200409655
58 h	14.99375275556790	-11.44920754480009	-2.06373220823979
59 h	14.65312359338087	-12.05754269816516	1.16841948713629
60 h	14.04678432021047	-16.66586519439354	0.23259177830413
61 h	14.40114901101286	-16.05254557524322	-2.99704892598738
62 h	18.78855145377202	-14.44971090060053	-2.20802863195587
63 h	18.43347261726680	-15.07032383465109	1.01800401001864
64 h	20.80482406746770	-18.56701829701717	-1.08489011204021
65 h	17.90031013890157	-19.70992049903114	0.07950332530809
66 h	18.25938170056301	-19.08350893929993	-3.17103037387029

67 h	-16.66214094892216	11.13688590853148	0.19000713718098
68 h	-17.20086421856742	15.98978214790578	0.56842841570423
69 h	-10.11935823539799	25.46918988292792	1.74287512423530

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14.2 Cartesian coordinates of T_2

ATOM	CARTESIAN COORDINATES		
1 c	-2.14065597270484	6.30477440706311	-2.62442081497908
2 c	0.53102415108127	6.19064663754087	-2.50947411665494
3 c	1.90630831765689	8.44095090297452	-2.57313837775492
4 c	0.66558305749638	10.73817445551848	-2.75137739005775
5 c	-1.98062547107643	10.89529394231427	-2.86602103830735
6 c	-3.34667323762132	8.60715119899743	-2.79863620557474
7 o	1.55754536056205	3.86535291545619	-2.37152657921789
8 c	4.25108829918040	3.59572314540889	-2.36372511160759
9 c	4.86799477980117	0.79943658037094	-2.25287113652557
10 c	7.71769205523712	0.30948401346491	-2.26041152563997
11 c	8.39061992188418	-2.49788499742450	-2.11181512966763
12 c	11.23694719519577	-2.99988215916557	-2.12278339034904
13 c	11.92041463004353	-5.80240012804544	-1.94381294711072
14 c	14.76778179359098	-6.30061444559156	-1.95219198789196
15 c	15.45782910449889	-9.09984442154148	-1.74889418261055
16 c	18.30593504902325	-9.59416235726616	-1.75332503677998

17 c	19.00012899785812	-12.39086328753325	-1.53529926582571
18 c	21.84827108969001	-12.88498549565762	-1.53733177690146
19 c	22.52295697949295	-15.68375597844532	-1.31548882287310
20 c	-3.06860283349772	13.38965753187342	-3.04412219718410
21 c	-5.50606181716462	14.22685114001196	-3.08701293548225
22 c	-6.17793582137885	16.89155088755003	-3.28706085174860
23 c	-8.59207823203735	17.90217086764738	-3.26734134425865
24 c	-8.65875782587892	20.53820722289672	-3.48334641579128
25 c	-6.28763960536948	21.63074610662813	-3.68152012469149
26 s	-3.95285311508961	19.27480061348901	-3.59282339491047
27 c	-5.47907625875198	24.18565043597284	-3.93276619634751
28 h	-3.45646464754316	24.46565178311343	-4.05956739557099
29 c	-6.87738187628869	26.34934514154902	-4.03729381463744
30 h	-1.65443051236166	14.87008405995771	-3.15010027808665
31 c	-5.68127600163542	28.86357649950051	-4.31071481548603
32 o	-6.82498717605570	30.82974660914753	-4.41036626236003
33 o	-3.12068666924334	28.75262804798638	-4.44210664860149
34 o	-3.53721123035675	4.13783557338219	-2.71862558994165
35 c	-3.89416732874117	2.82208839423144	-0.36375741951726
36 c	-5.42740871747296	0.46042389563297	-0.88572258491828
37 c	-5.95474476023069	-1.06671065842783	1.51059067521160
38 c	-7.48552222272410	-3.46693977011007	1.01407844656839
39 c	-8.02004891502455	-5.01054267516327	3.39698554555643

40 c	-9.53978385054126	-7.41699695334743	2.89971516177917
41 c	-10.07070619467653	-8.96616534784257	5.28025906434182
42 c	-11.58139273532273	-11.37793533113421	4.78123387360881
43 c	-12.10733312606535	-12.93098148196575	7.16041907908533
44 c	-13.61255944364903	-15.34564497223496	6.66109963445592
45 c	-14.13510396787244	-16.90243055192171	9.03869699153906
46 c	-15.64016770767925	-19.31068659057385	8.52012344541653
47 c	-7.62339225508769	12.55789574208746	-2.91542050558511
48 n	-9.38898521183133	11.28725177422576	-2.77337031656897
49 c	-9.56282005888091	26.36361840254417	-3.89138046713791
50 n	-11.73756750939685	26.29349170989924	-3.76513820155192
51 h	3.94403378116289	8.40869380012485	-2.49961231436888
52 h	1.77311945226198	12.45756991152101	-2.80466442055110
53 h	-5.38175812773075	8.57623600970432	-2.91154469784604
54 h	5.02868745377775	4.45403942783617	-4.07749083200108
55 h	5.03911974734007	4.58752174046800	-0.72780857415270
56 h	4.01777471699025	-0.00441322264184	-0.55063647400105
57 h	3.98094562257374	-0.14168840654305	-3.86278905679985
58 h	8.55257160049591	1.11920500771418	-3.97235822660914
59 h	8.59389461207093	1.30113891961012	-0.66859873496563
60 h	7.55967436492729	-3.30625206741818	-0.39741276745713
61 h	7.51233991246298	-3.49452557547580	-3.69867475678399
62 h	12.06355000973864	-2.20443575141208	-3.84596520276726

63 h	12.11442433474047	-1.98370442706140	-0.54676633062285
64 h	11.09400011403610	-6.59606719509901	-0.21969810248768
65 h	11.04372309803581	-6.82125012378851	-3.51829054793756
66 h	15.59190478863313	-5.51877373079413	-3.68288170069104
67 h	15.64454947917464	-5.26815883638497	-0.38631230691009
68 h	14.63287141934401	-9.88069735692750	-0.01813754436335
69 h	14.58298223928497	-10.13409124575485	-3.31452794416132
70 h	19.12964074710269	-8.82062159123202	-3.48805159108981
71 h	19.18087372902054	-8.55183467662320	-0.19287524379518
72 h	18.17717043570054	-13.16592935102280	0.19939738665805
73 h	18.12773905343900	-13.43576144153259	-3.09568655369763
74 h	22.67063177864308	-12.11365111244225	-3.27167828944606
75 h	22.72039825693709	-11.84065007646551	0.02107265805888
76 h	24.56515466494587	-15.97229058073716	-1.32312567940687
77 h	21.78286608487935	-16.49241648208672	0.43372009377110
78 h	21.73198945730557	-16.76783607501196	-2.88432092364256
79 h	-10.26094509822531	16.74007883721586	-3.09683779233320
80 h	-10.38599856481690	21.61988233657543	-3.49522465380976
81 h	-2.54170044148543	30.47704218893324	-4.61699480274000
82 h	-2.05593796022860	2.34426160564449	0.44842137695618
83 h	-4.88779013775206	4.07335389642101	0.95289758467540
84 h	-7.20647271616502	1.00916577144620	-1.78108078738072
85 h	-4.40525318513743	-0.70121476150874	-2.25466838187741

86 h	-4.16288284961244	-1.57939512735778	2.41290569701101
87 h	-6.96768768289767	0.11565874604529	2.87438190842686
88 h	-9.27770090845741	-2.95613077170406	0.11315192465883
89 h	-6.47471832365804	-4.64788388871565	-0.35281166665817
90 h	-6.22607677092762	-5.51257336887418	4.30183375217188
91 h	-9.03682479909891	-3.83053554959031	4.76072339406903
92 h	-11.33461371908448	-6.91546594507069	1.99732468410809
93 h	-8.52377597783596	-8.59439801422751	1.53291127058416
94 h	-8.27530619417149	-9.46193849830062	6.18560911471343
95 h	-11.09214498902319	-7.79114626119673	6.64494733029806
96 h	-13.37810956631584	-10.88260414683080	3.87883946714111
97 h	-10.56096743564015	-12.55071937514805	3.41371170919958
98 h	-10.31022622429144	-13.42310988669866	8.06438513289501
99 h	-13.13089008125889	-11.75971311195202	8.52686778442425
100 h	-15.41199562558042	-14.85555934959799	5.76042210829823
101 h	-12.59136625931142	-16.51731541418691	5.29270280581438
102 h	-12.33772099183868	-17.39395172728225	9.93810107740363
103 h	-15.15648997450956	-15.73316162313588	10.40575963291754
104 h	-15.98023570393866	-20.37770272426796	10.25209848019037
105 h	-17.47651975527877	-18.87671530464312	7.68203787898070
106 h	-14.63679285383217	-20.54980730195983	7.20846697829562

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14.3 Cartesian coordinates of T_3

ATOM	CARTESIAN COORDINATES		
1 c	-6.58334169475210	0.12864521250019	0.96021569363753
2 c	-3.96054658656253	0.24921073113363	0.58358219751832
3 c	-2.81315184812192	2.60256944800908	0.22830515251704
4 c	-4.28480341764830	4.76514127559472	0.25991059228897
5 c	-6.91310896363772	4.69266781953012	0.64419847213676
6 c	-8.02619183603096	2.29043061448176	0.99228816638011
7 o	-2.73003587646749	-1.97996540093686	0.59473654214725
8 c	-8.23208047257816	7.07752576053596	0.64943774509729
9 c	-10.70710393976896	7.69960708277875	1.02216755143966
10 c	-11.62952636579796	10.29300921830326	0.93828804380149
11 c	-14.08376939394044	11.09224930827382	1.40313956666952
12 c	-14.42735559103682	13.70125499810253	1.19877506516918
13 c	-12.24045362617431	15.00618286592633	0.55766653642306
14 s	-9.72308817921329	12.84465092414838	0.21734955462152
15 c	-11.62344907912654	17.57634350471486	0.12264255782658
16 h	-9.65612446878791	17.87941441661625	-0.38368762113499
17 c	-12.91824610894334	19.82042823416117	0.17963970120914
18 h	-6.99641567210952	8.67599840679993	0.29886791480562
19 c	-15.59863261053705	20.15574886105792	0.80105590398943
20 n	-16.47491208493058	22.63809118346055	0.73998490560606
21 c	-15.13928197898988	24.80470190993515	0.16283363278299

22 n	-12.62916462373343	24.37805680355087	-0.41047411281803
23 c	-11.36997675010352	22.07482108115013	-0.45799047062833
24 o	-9.13799603680945	22.01714131530206	-1.00255861313444
25 o	-16.08319388010942	26.88689789377116	0.15931600749217
26 o	-17.07859320438968	18.48067221927900	1.35413504821519
27 c	-12.60902991497464	5.85335756996515	1.54322770210975
28 n	-14.20017354154542	4.42529112451246	1.96912316787427
29 c	19.48075583430111	-20.06906518707645	-0.37547868805466
30 c	18.62187817119101	-17.31796143751093	-0.54286898735527
31 c	15.76661006710903	-16.99042879597455	-0.23383380008880
32 c	14.88693493834754	-14.24357202115690	-0.39795546004800
33 c	12.03075919955577	-13.92025312397410	-0.09303529944197
34 c	11.14957619094188	-11.17322586240559	-0.25260266954729
35 c	8.29264498708434	-10.85481345768676	0.04988105258978
36 c	7.40847722096079	-8.10830856707065	-0.10210842542343
37 c	4.55145285313552	-7.79832256364541	0.20457074455415
38 c	3.66432413568846	-5.05170654914284	0.06191695553311
39 c	0.80511543561310	-4.76924795937981	0.38469836469267
40 c	-0.04517941184691	-2.03657845248211	0.25074880690914
41 h	-7.44336704472971	-1.70574842367980	1.22679744633096
42 h	-0.80201332402453	2.76024527725052	-0.07041715017136
43 h	-3.37399692963913	6.57679977328078	-0.01801160888261
44 h	-10.03458050270890	2.11338010540580	1.28855841406850

45 h	-15.58128107240988	9.79173008284668	1.88415353430701
46 h	-16.19230082104677	14.66665175897074	1.49797501350113
47 h	-18.31782654020507	22.88670555198108	1.16735492464740
48 h	-11.59521070485716	25.92220123944818	-0.84241310271554
49 h	21.52351292763705	-20.23929313421792	-0.60434214442961
50 h	18.98471267029813	-20.89524395212276	1.45035491507296
51 h	18.58893110636714	-21.21876423854976	-1.83991220073449
52 h	19.20438620538145	-16.52426281686958	-2.36230562975550
53 h	19.59475915984581	-16.20348547277588	0.90326162189179
54 h	15.18408892280765	-17.78679534110453	1.58670340134104
55 h	14.79376080625357	-18.10714301867857	-1.68099197557863
56 h	15.47339523609693	-13.44755087275891	-2.21712180906987
57 h	15.85842070007294	-13.12915090397669	1.05158985206846
58 h	11.44425894478680	-14.71909148697404	1.72477919582890
59 h	11.05964041616710	-15.03276145113542	-1.54411403638498
60 h	11.73731101957314	-10.37257911478396	-2.06923932607919
61 h	12.11786110543488	-10.06115498010928	1.20076417981439
62 h	7.70511881853982	-11.65957898017364	1.86464282855813
63 h	7.32446153633161	-11.96384604694590	-1.40564207231369
64 h	7.99294837819323	-7.30222670786362	-1.91732050285707
65 h	8.37596860163782	-6.99892839829127	1.35373247844424
66 h	3.96670345250848	-8.60734247495036	2.01764858890766
67 h	3.58245931547189	-8.90249455359975	-1.25321238967758

68 h	4.24038687017301	-4.24391445459480	-1.75478357237093
69 h	4.63704594886692	-3.94726475990648	1.51746775897498
70 h	0.21779094245715	-5.55675852834594	2.20166535845539
71 h	-0.18263112684768	-5.84498519367272	-1.07593587085312
72 h	0.43107717896235	-1.20300850614357	-1.58197583485057
73 h	0.86038070601098	-0.90969098145996	1.73058423914342

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14.4 Cartesian coordinates of T_4

ATOM	CARTESIAN COORDINATES		
1 c	-1.82591955723368	5.23056453090286	-2.51353311834826
2 c	0.84652579975503	5.08781582492628	-2.44128840211067
3 c	2.24526042066215	7.32392219557058	-2.50988797070379
4 c	1.02736908124271	9.63507081171813	-2.64541406701731
5 c	-1.61908860915175	9.82130741266266	-2.70580521360207
6 c	-3.00963569419457	7.54750245995496	-2.64040554282293
7 o	1.85287489105110	2.75248545944542	-2.33630455509506
8 c	4.54521779398021	2.46604996111927	-2.32318457732074
9 c	5.15221300163162	-0.33074532281013	-2.18334949889288
10 c	8.00222413813554	-0.81857213827691	-2.15504120181378
11 c	8.68259404354931	-3.62021006957195	-1.94912583708818
12 c	11.53161249776809	-4.10430316837174	-1.90328223631274
13 c	12.23346107362167	-6.89639369629840	-1.65199497659187

14 c	15.08490086658297	-7.36634311576487	-1.59124921066007
15 c	15.79963829826678	-10.15223811608591	-1.30934757043233
16 c	18.65245854839947	-10.61265103947756	-1.23966283259064
17 c	19.37439572046155	-13.39466854693373	-0.94180412546464
18 c	22.22755315657492	-13.85256638178721	-0.86885727576851
19 c	22.93120650165073	-16.63666603340614	-0.56791333041767
20 c	-2.67811447534906	12.32929386953368	-2.82515309112874
21 c	-5.10375504919516	13.20306023637547	-2.76969667241368
22 c	-5.73016823625181	15.88086513383206	-2.91412896429136
23 c	-8.12458950522273	16.93738321264844	-2.74374350727185
24 c	-8.15897431720390	19.57044612659734	-2.92249539693392
25 c	-5.78069931574796	20.63647531801996	-3.24776299624855
26 s	-3.48627256453243	18.21721671357164	-3.32776715269414
27 c	-4.83769526863422	23.12796166924764	-3.52455696837844
28 h	-2.80092061742241	23.21641634012207	-3.77619222312674
29 c	-5.87437933099888	25.50303713167056	-3.54987162156996
30 h	-1.24859615790055	13.79192359732650	-2.96290348712940
31 c	-8.55815955463560	26.12685027926204	-3.24914548656266
32 n	-9.14052995289733	28.69455903492174	-3.31565232349224
33 c	-7.51127392779963	30.70777985443706	-3.63813665918163
34 n	-5.01227957747265	30.01071668629838	-3.92255358217382
35 c	-4.01981392997275	27.57999372003174	-3.90952874769622
36 o	-1.75753244801148	27.28143468894585	-4.18330089734887

37 o	-8.21032947648663	32.88429547797955	-3.66927958063546
38 o	-10.27212314645995	24.61822580209382	-2.95102526870483
39 o	-3.24712724382105	3.08012018076685	-2.61226095784255
40 c	-3.57317915003191	1.72975017618392	-0.27233219467022
41 c	-5.14164304061333	-0.60653211967880	-0.80379185734129
42 c	-5.62202638866206	-2.17939250841919	1.57275330388656
43 c	-7.18995490417851	-4.55332164923948	1.06609866287056
44 c	-7.66142205637740	-6.15232069398124	3.42570621856447
45 c	-9.22170896504190	-8.53062714730098	2.91913997858227
46 c	-9.67525967445087	-10.14304021168258	5.27359353262311
47 c	-11.23205865034981	-12.52360112070877	4.76710417161974
48 c	-11.66968419787029	-14.14545432138972	7.11816868189788
49 c	-13.22598011895554	-16.52618859588086	6.61324828616035
50 c	-13.65354590192778	-18.15503226049676	8.96145146796994
51 c	-15.21245710571544	-20.52769647478677	8.43844707311944
52 c	-7.23768510574239	11.56438655592965	-2.52749076281588
53 n	-9.01247240990035	10.31503250637178	-2.32379773939690
54 h	4.28333639462874	7.26958138735671	-2.47471646574690
55 h	2.15194685637324	11.34303450995891	-2.70437336025003
56 h	-5.04681392299302	7.54119508875388	-2.71715576224815
57 h	5.32980954646008	3.30543037697917	-4.04303400412553
58 h	5.33559065477474	3.46809909259458	-0.69493609335756
59 h	4.28458544262072	-1.11723961833036	-0.48177214189853

60 h	4.28091402319850	-1.28638952872199	-3.79329360587056
61 h	8.85354102158588	-0.03610290554380	-3.87149621859895
62 h	8.85991625762840	0.20215378205965	-0.57146107566226
63 h	7.82766479033078	-4.40307043605837	-0.23466011921171
64 h	7.83551038621938	-4.64826009949465	-3.53290814195416
65 h	12.38175045191661	-3.33937174659056	-3.62880672341462
66 h	12.37555196901088	-3.04851015281383	-0.33491519062168
67 h	11.37899773961542	-7.66089022693318	0.07165078249245
68 h	11.39816366038743	-7.95616283963630	-3.22200294422666
69 h	15.93697766517352	-6.61523411396824	-3.32201476140845
70 h	15.91880195161693	-6.28948272130612	-0.03177505650601
71 h	14.94507489765561	-10.90302672756194	0.42037109069790
72 h	14.97113037252501	-11.23155840118720	-2.86982685902980
73 h	19.50579218009310	-9.86887981647235	-2.97309898498600
74 h	19.48026964131176	-9.52447686792652	0.31529011375291
75 h	18.52180184425086	-14.14006764728319	0.79160942315318
76 h	18.54991868426120	-14.48568763506244	-2.49675228812353
77 h	23.07953509225107	-13.11026340653424	-2.60158858941158
78 h	23.05141315468923	-12.76215674499984	0.68432293868889
79 h	24.97644201666702	-16.89923677669234	-0.52378172358016
80 h	22.16198376294113	-17.41478114410893	1.18255322353824
81 h	22.18891593055869	-17.76601142273397	-2.12863920934068
82 h	-9.80064963728195	15.80102977180319	-2.48822211595449

83 h	-9.83434810019216	20.71941321150624	-2.82310663202747
84 h	-10.98373831304503	29.14120424716189	-3.10706523436998
85 h	-3.76807615028903	31.43656602581475	-4.16470045270597
86 h	-1.72533864866698	1.21860779499498	0.49596783251326
87 h	-4.52757017010257	2.96975294775827	1.08340897318446
88 h	-6.93730357581005	-0.02406164544625	-1.64274798010714
89 h	-4.16446959369251	-1.74821058286797	-2.22159612861752
90 h	-3.81230243724068	-2.72903069055815	2.41538180489855
91 h	-6.58614049947524	-1.01709743424812	2.98836036939647
92 h	-9.00502004543119	-4.00514625621467	0.23601528171373
93 h	-6.23391634400788	-5.70798863491857	-0.36143153869002
94 h	-5.84358578736397	-6.69466920782031	4.25631110724450
95 h	-8.61962472128911	-4.99822030125544	4.85271591817188
96 h	-11.04467463199509	-7.98866014722183	2.10074742542294
97 h	-8.26948605046221	-9.67692236370386	1.48164376763572
98 h	-7.85091329796082	-10.68347749520793	6.09091929547854
99 h	-10.62769004754934	-8.99798389751214	6.71184551174779
100 h	-13.06090594655138	-11.98360271730199	3.96025972268262
101 h	-10.28474983178629	-13.66255571075761	3.32050468689096
102 h	-9.83991744846898	-14.68592660634249	7.92326899685587
103 h	-12.61560890858320	-13.00685379585789	8.56593360570329
104 h	-15.05995936997491	-15.98783066698633	5.81607897515826
105 h	-12.28501389972877	-17.66282934868954	5.16023500091992

106 h -11.82144853651474 -18.69618587720208 9.75588218567961

107 h -14.59297287131878 -17.02038200437003 10.41395661125954

108 h -15.48153103797851 -21.64811550192076 10.14904726529737

109 h -17.08153866649318 -20.04564654902633 7.70574082473288

110 h -14.28980617701688 -21.73348826002210 7.03928853281539

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