Electronic Supporting Information

Efficient Molecular Solar Thermal Energy Storage in Self-Assembled Columnar Triethynylbenzene–Azobenzene Systems

Ashy,[a] Rankit Talukdar,[b] Kiran,[a] Shreya,[a] and Monika Gupta[,a]*

[a]Department of Chemistry, Indian Institute of Technology Jodhpur, Karwar, Jodhpur, Rajasthan 342030, India

[b]Department of Chemistry, Indian Institute of Technology Ropar (IIT-Ropar) Bara Phool, Punjab-140001, India

*[,a]*Corresponding author: Tel.: +91-291-280-1315; E-mail: mgupta@iitj.ac.in*

Table of Contents

1. Experimental Section

1.1. Materials and Reagents

Chemicals and solvents were all of AR quality and were used without further purification. Chemicals were purchased from Sigma-Aldrich (Bangalore, India), TCI, and Avra Synthesis Pvt. Ltd. Column chromatographic separations were performed on silica gel (60-120, 100-200 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254).

1.2. Synthesis and Characterization of Target Compounds (3-6)

For synthesis of compound **3**, compound **1** (2 g, 1equivalent) was added to a 1:1 solution of conc. HCl (3.57 equivalents) and water at 0 °C and stirred for 15 minutes. An aq. solution of $NaNO_2$ (0.7 g, 1.07 equivalents) was added dropwise to the mixture at 0 °C, and the solution was stirred for 40 minutes at room temperature. A solution of compound **2** (1.2 g, 1.006 equivalents) in 10% aq. NaOH (0.89 g, 2.32 equivalents) was then added to the mixture at 0 °C. The resulting mixture was further stirred for 1 hour at room temperature. After the completion of reaction, the organic layer was extracted with DCM and dried over Na_2SO_4. It was further concentrated under reduced pressure and purified by column chromatography to get the pure compound **3**.

Compound 3 (Yield: 50%)

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.23 (d, $J = 8$ Hz, 1H), 6.78 (s, 1H), 6.56 (d, $J = 12$ Hz, 1H), 6.22 (d, $J = 8$ Hz, 1H).

For the synthesis of compound **5,** compound **3** (1 g, 1equivalents) was added in dry single neck round bottom flask of 50 ml under argon and dissolved in butanone (25 ml). This was followed by addition of K_2CO_3 (1.18 g, 3 equivalents) and the mixture was stirred for 15 minutes. To the stirred mixture, 1-bromodecane (0.76 g, 1.2 equivalents) and catalytic amount of KI was added. The progress of the reaction was monitored by TLC. After the completion of the reaction (18 hours), the mixture was diluted with water. The organic layer was extracted with dichloromethane and was dried over anhydrous sodium sulphate followed by evaporation of the solvent. The crude mixture was purified by column chromatography using silica gel (100-200), DCM and Hexane as eluents to obtain 28% of compound **5**.

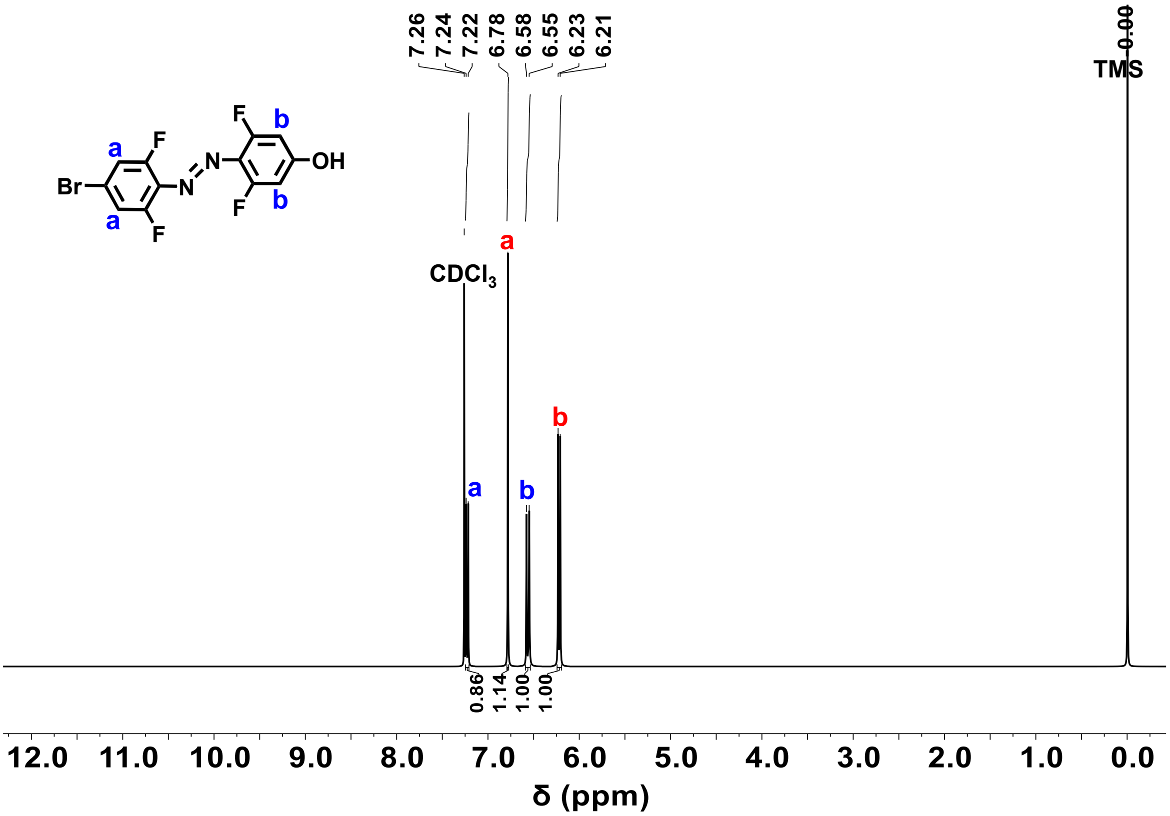

Figure S1. ^{1}H NMR of azobenzene **3** (***E***, ***Z***).

Compound 5 (yield: 28%)

^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm): 7.23 (d, J = 8 Hz, 1H), 7.07 (d, J = 4 Hz, 1H), 6.57 (d, J = 12 Hz, 1H), 6.39 (d, J = 8 Hz, 1H), 4.00 (t, J = 8, 4 Hz, 1H), 3.89 (t, J = 4, 8 Hz, 1H), 1.81 - 1.74 (m, 2H), 1.45 - 1.26 (m, 14H), 0.88 (t, J = 4, 8 Hz, 3H).

For the synthesis of three-arm star-shaped final compound **6**, an oven-dried double neck round bottom flask of 50 ml was filled with anhydrous THF (25 ml) under argon. The flask was purged with argon gas and back-filled three times. Then triethylamine (2ml) was added, stirred for 10 minutes. After the addition of bis-(triphenylphosphine)-palladium-(II) chloride (0.1 g, 0.11 equivalent) in the mixture, it was stirred for 5 minutes. To the stirred mixture, compound **5** (0.68 g, 4 equivalents) and Copper iodide (0.05 g, 0.2 equivalent) was added respectively. After few minutes of stirring, compound **4** (0.2 g, 1 equivalent) was added little by little. Next the reaction mixture was kept for refluxing at 70 ˚C for 18 hours. The progress of the Sonogashira Coupling reaction was monitored by TLC. After cooling, the resulting mixture was extracted with DCM. The solvent was evaporated in rotary evaporator, and the final product was purified by column chromatography using silica gel (230-400), DCM and Hexane as eluents. The produced compounds' structural characterization was done *via* elemental analysis, mass spectrometry, ^{1}H and ^{13}C NMR and UV-Vis spectroscopy.

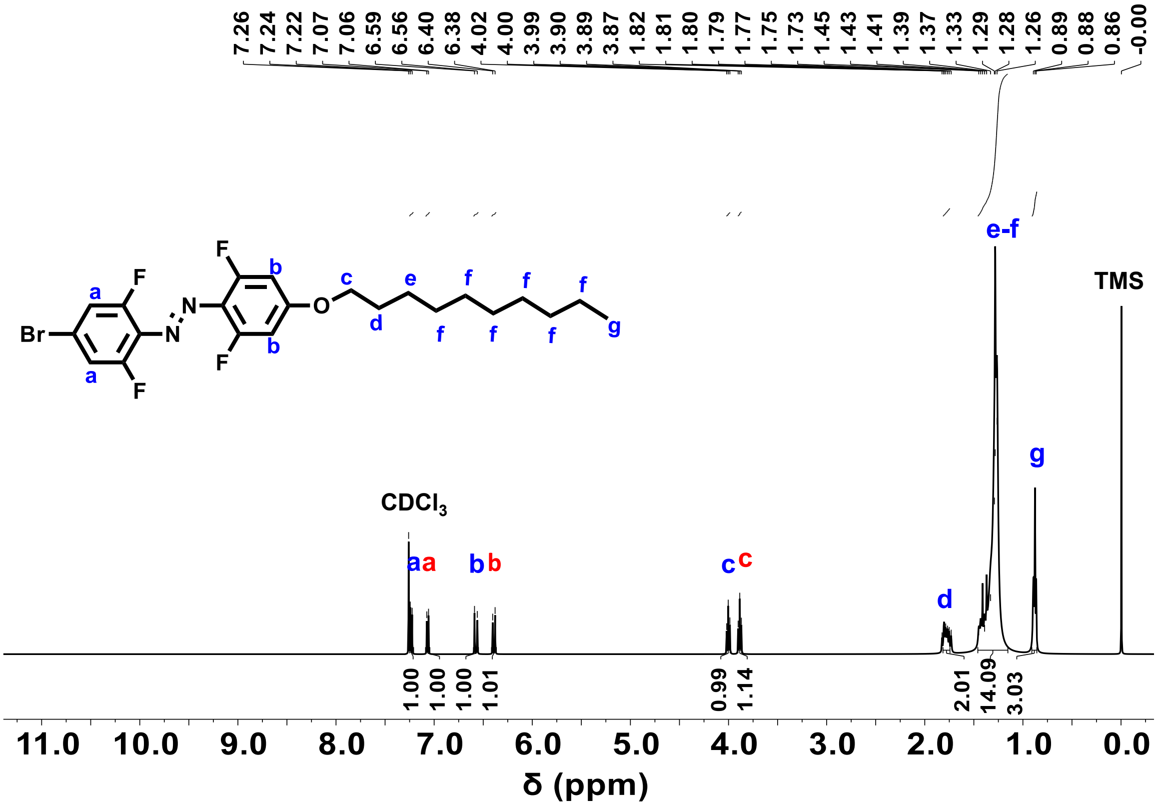

Figure S2. ^{1}H NMR of alkylated azobenzene **5** (***E***, ***Z***).

Compound 6 (yield: 5.5%)

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.65 (s, 1.50H), 7.59 (s, 1.49H), 7.19 (s, 1.94H), 7.03 (s, 4.03H), 6.59 (d, J = 12 Hz, 2.73H), 6.40 (d, J = 12 Hz, 3.27H), 4.01 (t, J = 8, 4 Hz, 2.41H), 3.89 (t, J = 4, 8 Hz, 3.50H), 1.83 - 1.71 (m, 5.60H), 1.42 - 1.28 (m, 42.01 H), 0.87 (t, J = 8 Hz, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 162.64, 158.62, 156.53, 156.29, 154.18, 147.58, 147.04, 138.42, 134.94, 132.28, 125.94, 124.44, 123.96, 123.33, 119.07, 115.89, 99.37, 90.66, 88.67, 69.24, 40.87, 34.84, 34.49, 31.87, 31.40, 30.15, 29.69, 29.51, 29.29, 28.80, 25.83, 22.66, 19.13, 14.10.

MS: m/z Calculated for $C_{78}H_{78}F_{12}N_6O_3$ 1375.4731. Found 1375.4942.

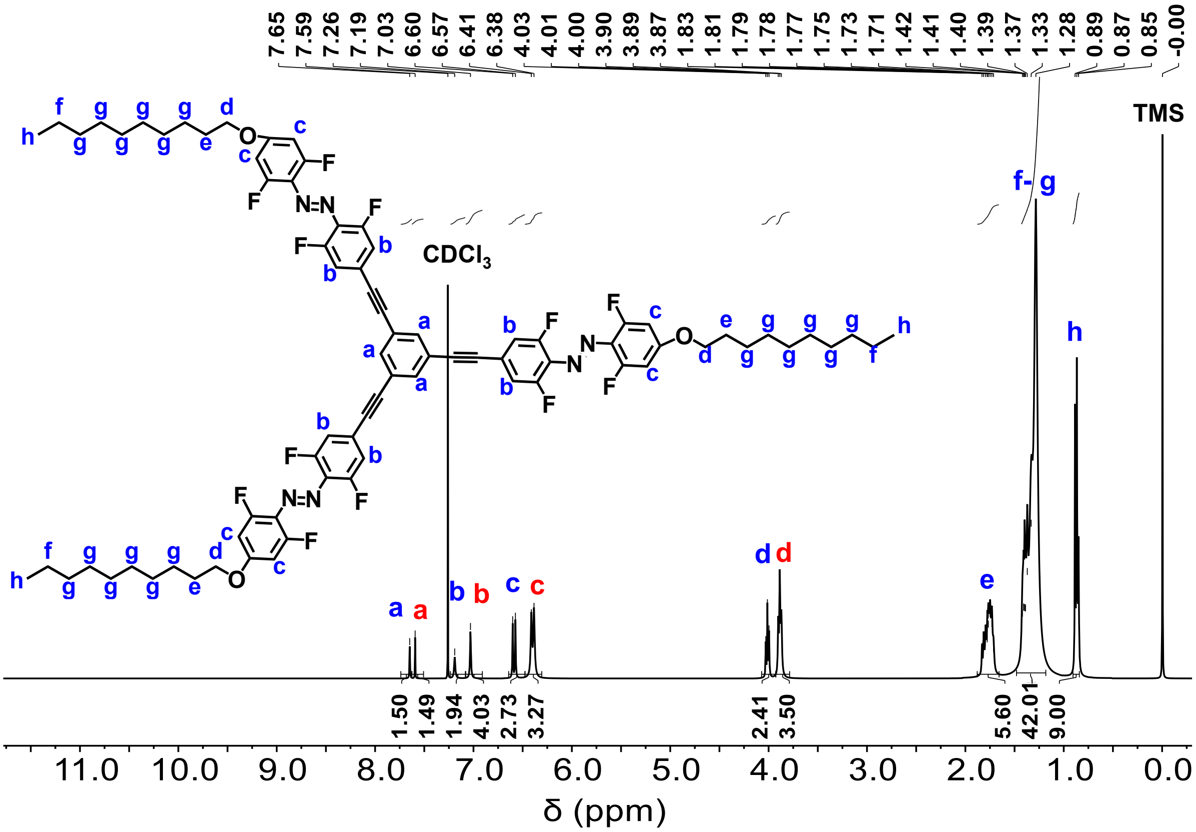

Figure S3. ^{1}H NMR of final compound **6** (***E***, ***Z***).

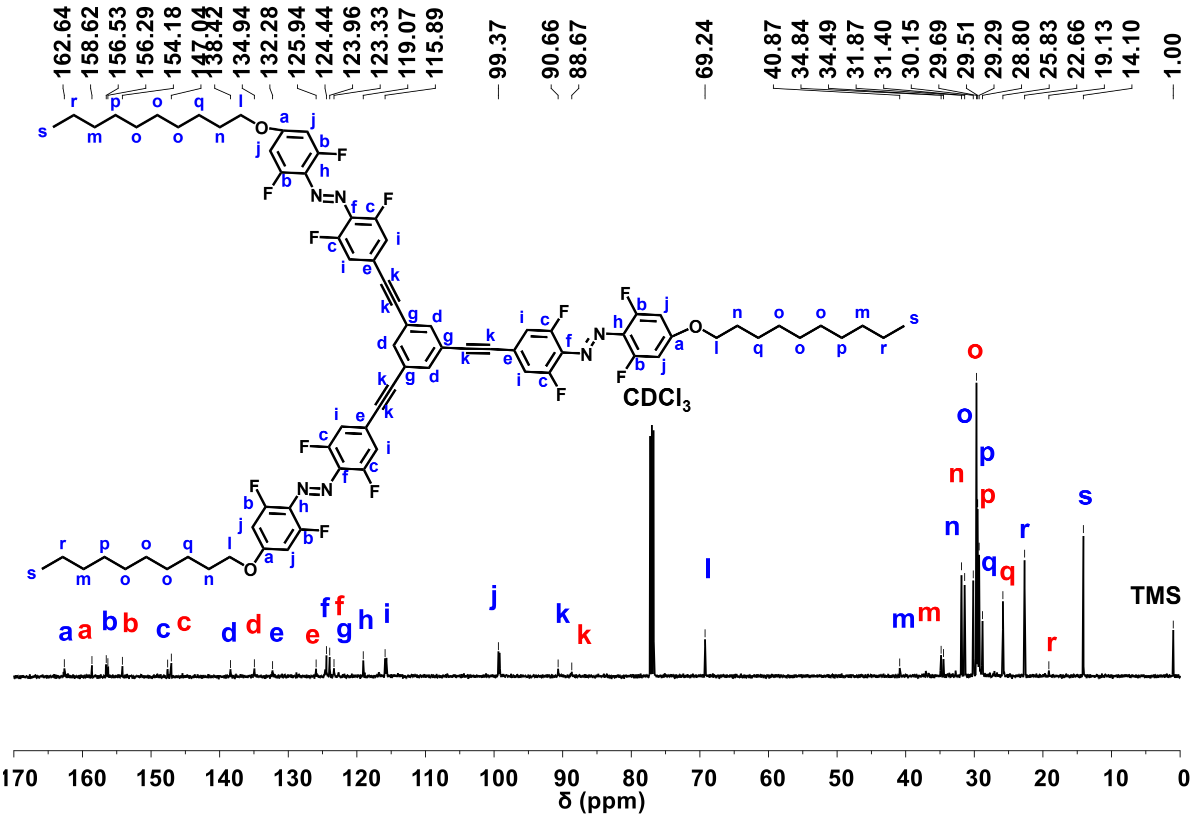

Figure S4. ^{13}C NMR of final compound **6** (***E***, ***Z***).[1]

1.3. Instrumental

1.3.1. Structural characterization. Structural characterization of the compound was carried out through a combination of ^{1}H NMR and ^{13}C NMR (Bruker AVANCE III HD, Ascend TM WB, 500 MHz spectrometer) and UV-Vis spectroscopy (Jasco V730). NMR spectra were recorded using deuterated chloroform ($CDCl_3$), methanol (MeOD) and DMSO-D_6 as solvent and tetramethylsilane (TMS) as an internal standard. HRMS spectra were recorded on a Finnigan MAT 95 using EI ionization at 70 eV of using Agilent 6500 Q-TOF spectrometer.

1.3.2. Differential Scanning Calorimetry. DSC was recorded on a DSC-4000 Perkin Elmer instrument with a thermocouple based precisely machined disc of chrome alloy as sensor with pyris software.

1.3.3. Polarized Optical Microscopy. Textural observations of the mesophase were performed with Nikon LV100N Pol Eclipse polarising microscope equipped with a Nikon Digital DS-Fi3 Camera and provided with a Hexon heating stage (RHX300 HC).

1.3.4. X-ray Diffraction. The temperature dependent WAXS investigations were performed on a Bruker Nanostar (Detector Vantec 2000, Microfocus copper anode X-ray tube Incoatec). Aligned samples were prepared by fiber extrusion method with a customized extruder. The aligned fibers were transferred to Mark capillaries, which were sealed and glued into the metal sample holder. The XRS heating system was calibrated by liquid crystal standard compounds. The XRS data was evaluated by the program datasqueeze using silver behenate as a calibration standard.

1.3.5 SEM Imaging. SEM Images were obtained from a Carl Zeiss Evo 18 Scanning electron microscope.

1.3.6. LED Irradiation. Photo irradiation studies was carried out using Holmarc HO-HBL-XY LED irradiation setup with 365 nm, 395nm, 430 nm, 530 nm, 590 nm and 625 nm LED lights having a power of 36 mW/cm^2.

1.3.7. IR Thermal Imaging. IR Thermal Images of heat release from thin film samples were captured using FLIR One Edge Pro thermal camera in MSX mode.

1.3.8. Thin film preparation. For thin film preparation, 100 µL of 15 mg/mL solution of DCM was drop-casted on each glass substrate measuring around 1.5 cm^2, followed by annealing at 60 °C for 30 minutes to acquire a Col$_h$ mesophase and to promote self-healing of the film.

2. Photophysical Studies

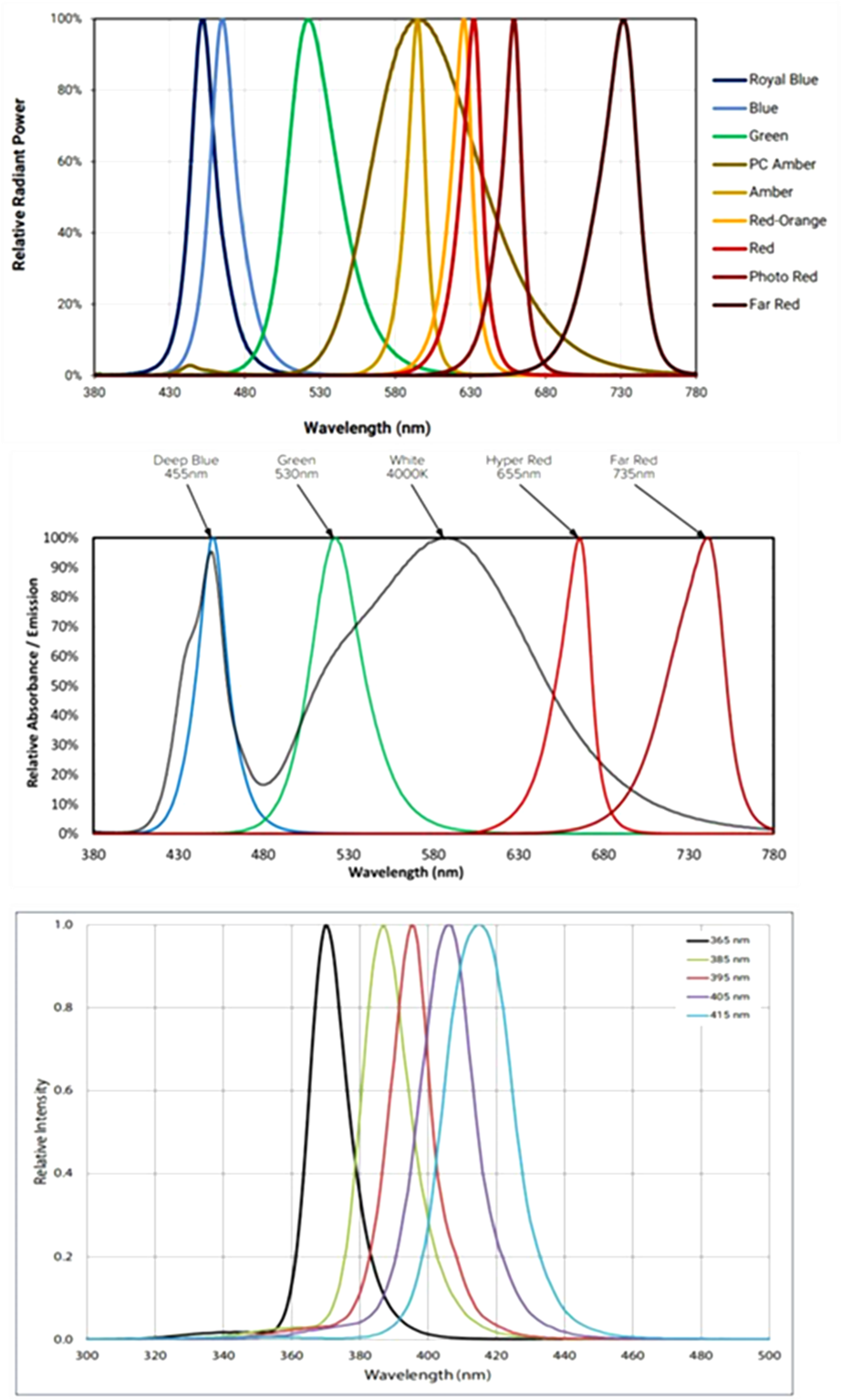

Figure S5. Emission Spectra of LEDs (as provided by Holmarc) used for the experiments.

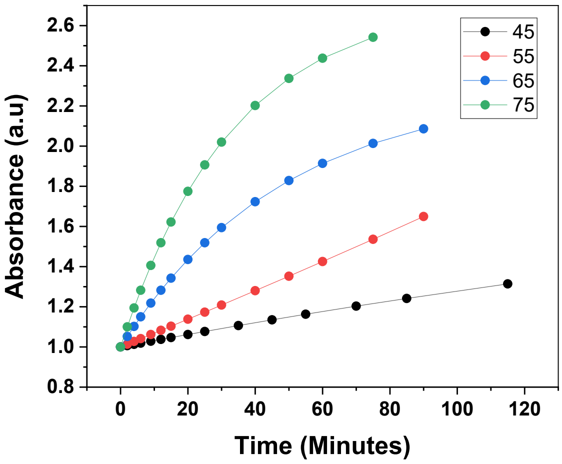

Figure S6. Absorbance at λ_{max} (344 nm) for thermal *Z* to *E* recovery of compound **6** (for 0.09 μM solutions) with time at different temperatures (as mentioned in the inset in °C).

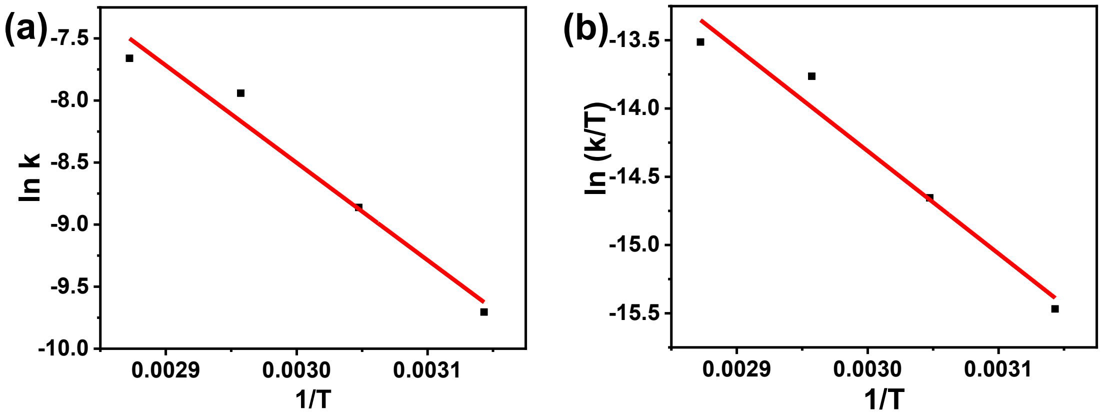

Figure S7. (a) Arrhenius and (b) Eyring-Polanyi plots for thermal *Z* - *E* isomerization of compound **6.**

Table S1. Half-life and other thermodynamic parameters calculated from Arrhenius and Eyring- Polanyi plots at 298K for compounds.

Compound	**$t_{1/2}$ [a] (hours)**	**E_a [b] (kJ/mol)**	**A [c] (s^{-1})**	**ΔH [d] (kJ/mol)**	**ΔS [e] (J/mol/K)**
6	15.25	65.24	3.3×10^6	62.48	-129

[a] Half-life of *Z* isomer at 298K
[b] Activation energy
[c] Arrhenius Constant
[d] Enthalpy of activation
[e] Entropy of activation

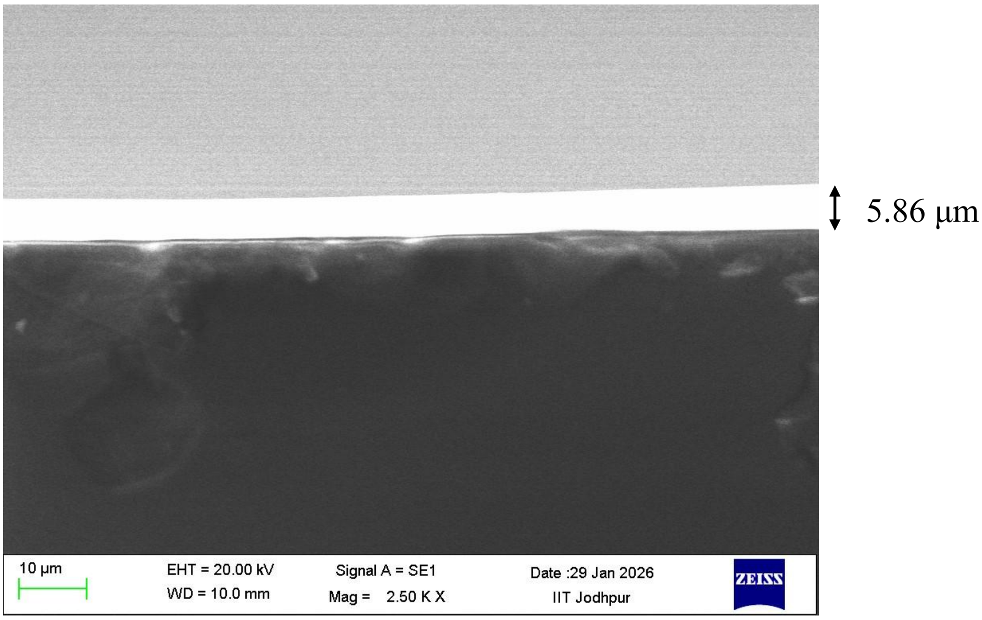

Figure S8. SEM image of a cross-section of the film of compound **6** showing the average thickness of the film.

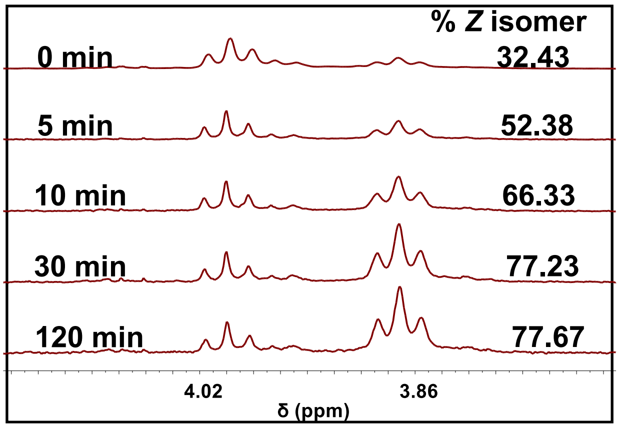

Figure S9. ^{1}H NMR of time-dependent increase of *Z* % on irradiation with 530 nm LED.

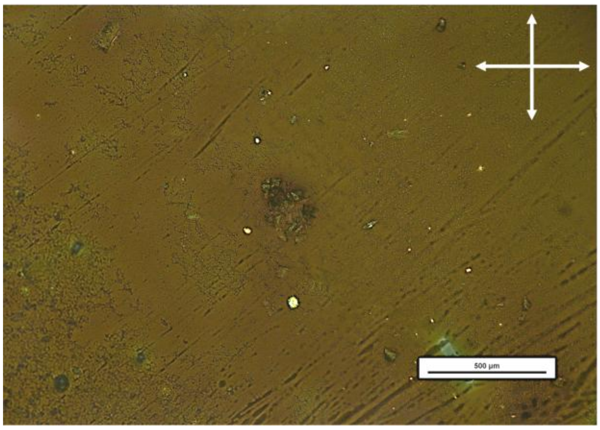

Figure S10. POM image of a *cis* rich thin film of compound **6**.

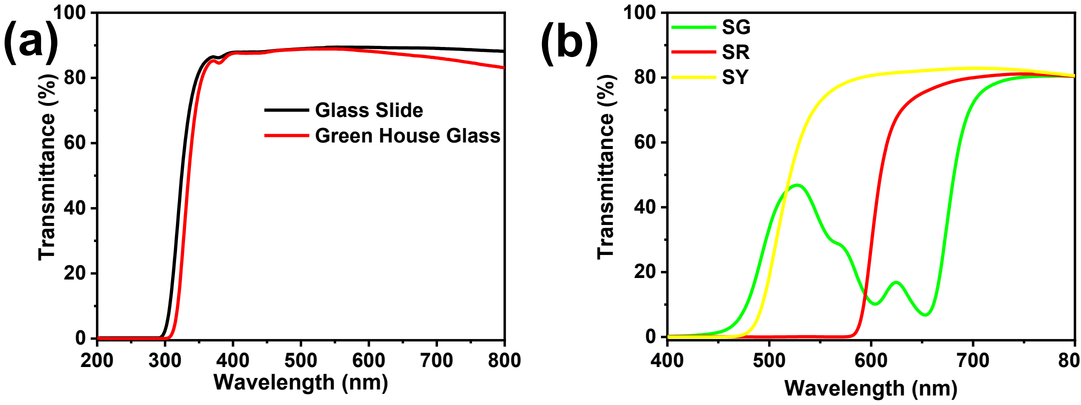

Figure S11. Transmittance spectra of (a) glass slide used for thin film preparation and green house glass. (b) band pass filters of Shopee of wavelengths green, red and yellow, used for solar irradiation experiments.

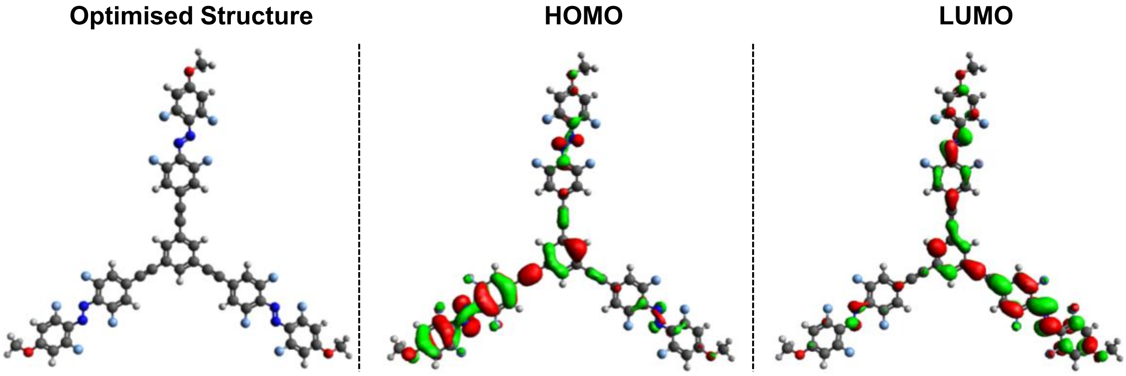

Figure S12. Optimized geometry and electronic distribution of frontier molecular orbitals (HOMO and LUMO) of final compound **6**.

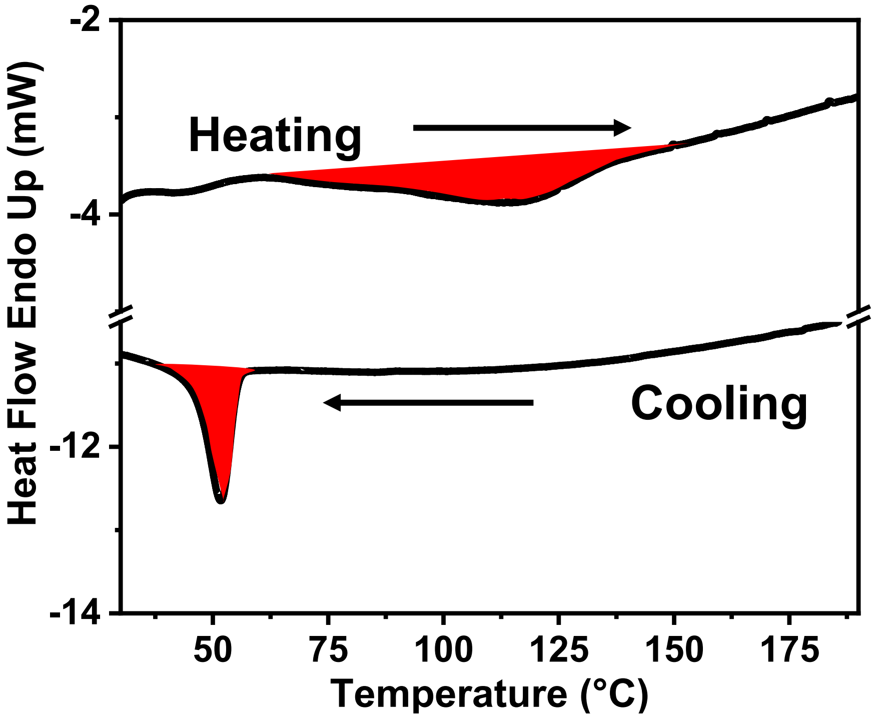

Figure S13. DSC thermogram of compound **6** in its *Z* PSS at the rate of 10 °C/min.

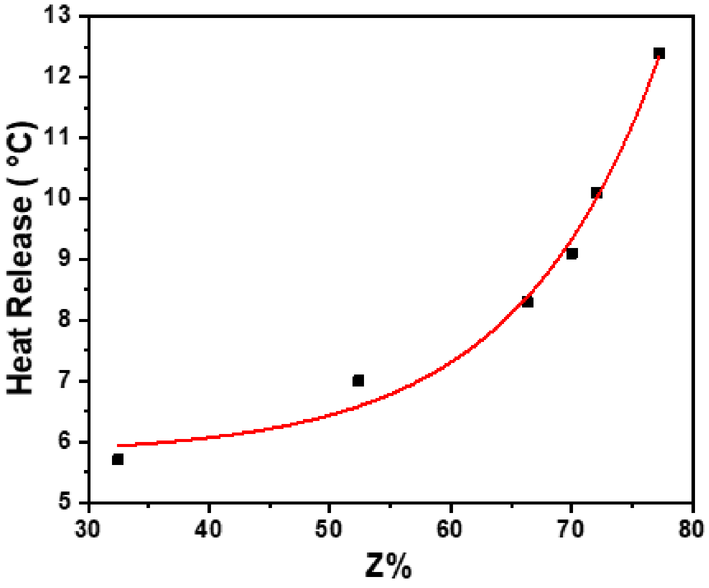

Figure S14. Quantitative analysis of heat release with respect to increasing %*Z* content in the charged films on irradiating them with 430 nm to induce *E* to *Z* isomerization.

Figure S15. IR Thermal images of glass substrate on 430 nm LED irradiation.

References:

1. A. Kerckhoffs, Z. Bo, S. E. Penty, F. Duarte and M. J. Langton, *Org. Biomol. Chem.*, 2021, **19**, 9058–9067.