Electronic supplementary information (ESI)

Through Structural Isomerism: Positional Effect of Alkyne Functionality on Molecular Optical Properties

Nakka Nagaraju, Dushyant Kushavah, Sunil Kumar, Rajeev Ray, Diksha Gambhir, Subrata Ghosh, and Suman Kalyan Pal**

School of Basic Sciences, Advanced Materials Research Center, Indian Institute of Technology Mandi, Kamand, H.P, 175005, India.

Experimental details

Materials and Methods:

3-Iodocarbazole, 1-bromohexane, potassium hydroxide, copper(I) iodide (CuI), triethylamine (Et_3N), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), 4-bromobnzaldehyde, trimethylsilylacetylene, potassium carbonate (K_2CO_3), piperidine, phosphoryl chloride ($POCl_3$), phenylacetylene, ammonium acetate (NH_4Ac), N,N-dimethylformamide (DMF), acetone, tetrahydrofuran (THF), methanol (MeOH), acetonitrile (ACN), dichloromethane(DCM) and acetic acid were purchased from commercial sources (TCI Chemicals and Merck) and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Jeol ECX NMR spectrometer. High resolution mass spectra were recorded on Bruker Maxis Impact HD instrument. UV–vis and fluorescence spectra were recorded on Simadzu UV-2450 and Perkin Elmer LS55, respectively. For the absorption and emission studies fresh stock solution (1mM) of the synthesized compounds were prepared using HPLC DCM. Thermogravimetric analysis (TGA) was done on a Perkin Elmer Pyris 1 and NETZSCH STA449 F1 JUPITER instrument under nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of degradation (Td) was correlated to a 5% weight loss. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane at room temperature on Metrohm Autolab electrochemical workstation. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum disc as working electrode, a platinum wire as auxiliary electrode, and Ag/AgCl as reference electrode. Ferrocenium–ferrocene (Fc+/Fc) was used as the external standard. Fluorescence decay kinetics were measured on a time correlated single photon counting (TCSPC) setup (Chronos BH Fluorescence lifetime spectrometer) from ISS, USA.

Femtosecond transient absorption (TA) was measured using a femtosecond pump-probe TA spectrometer fitted with a femtosecond laser from Spectra-Physics, USA. The laser comprises of a mode-locked Ti:sapphire oscillator (Mai Tai, Spectra-Physics), which generates femtosecond pulses of wavelength at 800 nm. The Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra-Physics) was used to amplify the oscillator output. The Ti:sapphire regenerative amplifier was pumped by 527 nm light from a frequency-doubled Nd:YLF laser (Empower, Spectra-Physics). The laser pulses (∼35 fs) centered at 800 nm and of energy ∼4 mJ were generated by the regenerative amplifier at a repetition rate of 1 kHz. Amplifier output was then cleaved into two constituents. One beam was sent to an optical parametric amplifier (TOPAS Prime, Spectra-Physics) which produces pump pulses. The second component was centered onto a moving CaF_2 and sapphire crystals through a delay unit for white-light continuum (WLC) (350−800 nm) generation. To achieve a large overlap between the pump and probe beams and to generate a TA spectrum of high signal-to-noise ratio, both beams of near collinear geometry were used. An adjustable neutral density filter was used before the sample (drop casted on quartz substrate, dye sample dip coated on TiO_2 spin coated substrate) to control the intensity of the incident excitation beam. Pump blocked and unblocked conditions with a 500 Hz mechanical chopper were utilized to detect the probe pulses. TA spectra measurements were accomplished by charge-coupled device arrays after dispersion by a grating spectrograph (Acton SpectraPro SP 2358). A chirp correction program was used to compensate the group velocity dispersion of the WLC spectra. TA kinetic traces measurements were completed by using two well-aligned photodiodes of variable gain by controlling the relative delay between the pump and probe pulses with the help of a stepper motor-driven optical delay line. MATLAB, Origin Lab and a software package provided by Pascher Instrument were used for analyzing the data.

Computational Details:

Density functional theory calculations have been carried out by using Gaussian 09 program employing B3LYP hybrid functional and 6-31 G (d,p) basis set to understand the spectral properties and for the analysis of molecular orbitals. The solvent (DCM) effect is introduced using polarized continuum (CPCM) solvation model. All calculations have been performed in gas phase. Electron density distribution of HOMO and LUMO levels were plotted using an isovalue = 0.03. Absorption spectrum of the dye cations were calculated with the time-dependent density functional theory (TD-DFT) following ground state geometry optimization.

The ionization potential (I_p) and electron affinity (E_a) values were computed using the following relations[1]

$$I_p = E^+(M) - E(M) \qquad (1)$$

$$E_a = E^-(M) - E(M) \qquad (2)$$

where $E(M)$, $E^+(M)$ and $E^-(M)$ denote the total energy of the neutral, cationic and anionic species at their respective optimized geometries. The total energies of different species were calculated by using a ΔSCF method.

Experimental determination of electron affinity:

In the case of organic molecules, the fundamental (or transport) gap (E_f) is not same as optical gap (E_o).[2] The difference between these two gaps is a measure of exciton binding energy (B_e), i.e.,

$$B_e = E_f - E_o \qquad (3)$$

Nonetheless, electron affinity (E_a) is related to the fundamental gap by the relation[2]

$$E_a = I_p - E_f = I_p - E_o - B_e \qquad (4)$$

In π-conjugated organic molecules,[3]

$$B_e = 0.3(E_f - 1\text{ eV}) \qquad (5)$$

By combining equations (3) and (5), we obtain

$$B_e = 0.43(E_o - 1\text{ eV}) \qquad (6)$$

We estimated exciton binding energy of CAPC and PACC using equation (6) and found to be 0.73 eV and 0.77 eV, respectively. The electron affinity of the dye molecules was determined from equation (4). The obtained values of E_a are 2.28 eV and 2.05 eV, respectively.

Synthesis of CAPC:

9-Hexyl 3-Iodo carbazole (2): To a 500 mL round bottom flask were added 3-Iodo carbazole (5.0 g, 17.0 mmol) and potassium hydroxide (2.86 g, 51.1 mmol) in acetone (70 mL) followed by 1-hexyl bromide (2.61 mL, 18.7 mmol). The reaction mixture was stirred for 8h at room temperature. Then, the acetone was removed under reduced pressure to get the crude product. The crude material was further purified by coloumn chromatography (Hexane : Ethyl acetate = 9:1 as the eluent) to get the compound 2 as a white solid. (6.05 g, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.28 (s, 1H), 7.89 (d, J = 7.55 Hz, 1H), 7.57-7.55 (m, 1H), 7.38-7.35 (m, 1H), 7.22 (d, J = 8.20 Hz, 1H), 7.15-7.12(m, 1H), 6.96(d, J = 8.25 Hz, 1H), 3.98 (t, 2H), 1.66-1.62 (m, 2H), 1.22-1.16 (m, 6H), 0.78 (t, 3H). ^{13}C NMR ($CDCl_3$ $^{\delta}$/ppm) 140.5, 139.7, 133.9, 129.3, 126.5, 125.5, 121.7, 120.7, 119.5, 110.9, 109.1, 81.5, 43.7, 31.8, 30.1, 29.1, 27.2, 22.8, 14.4.

***4- ((trimethylsilyl)ethynyl)benzaldehyde* (*4*):** Trimethylsilylacetylene (0.575 mL, 4.05 mmol) was added to a mixture of 4-bromobenzaldehyde (0.5 g, 2.70 mmol), $Pd(PPh_3)_2Cl_2$ (47 mg, 0.067 mmol) and CuI (12 mg, 0.067 mmol) in Et_3N (7 mL). The reaction mixture was stirred overnight at 80°C. After cooling to room temperature, the resulting ammonium salt was filtered off, and the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography with petroleum ether as eluent to afford 4- ((trimethylsilyl)ethynyl)benzaldehyde as a yellow semi solid after removal of the solvent (0.52 g, 95%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.01 (s, 1H), 7.88 (d, J = 7.55 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 0.33 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.0, 135.6, 132.4, 129.3, 129.2, 103.9, 98.8, 31.6, 22.6, 14.1.

***4-ethynylbenzaldehyde (5)*:** 4-((Trimethylsilyl)ethynyl)benzaldehyde (2.0 g, 10.0 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) were dissolved in the MeOH (30 mL). The reaction mixture was stirred at room temperature until reaction completion and then the solvent was concentrated under reduced pressure. The crude was dissolved in dichoromethane and washed with water, and then dried over sodium sulfate. The solvent was removed by rotary evaporation to give a light-yellow powder identified as 4- ethynylbenzaldehyde (**5**) (1.30 g, 67%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 7.88 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 3.36 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.5, 135.9, 132.7, 129.5, 128.3, 82.7, 81.2.

4-((9-hexyl-9H-carbazol-3-yl)ethynyl)benzaldehyde (6): A mixture of compound **2** (500 mg, 1.3 mmol), 4-ethynylbenzaldehyde (206 mg, 1.59 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 0.032 mmol), CuI (5 mg, 0.026 mmol) and Et_3N (0.362 ml) in tetrahydrofuran was stirred at 66 °C for 12 h under the anhydrous and anaerobic conditions. The mixture was cooled to room temperature. Precipitates were filtered off and concentrated to give the crude product. The crude material was purified by column chromatography (petroleum ether : dichloromethane = 4 : 1 as the eluent) to give the compound **6** as a yellow solid (260 mg 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.0 (s, 1H), 8.32 (s, 1H), 8.10 (d, J = 7.65 Hz, 1H), 7.85 (d, J = 8.25 Hz, 2H), 7.69 (d, J = 8.25 Hz, 2H), 7.66-7.64 (m, 1H), 7.51-7.48 (m, 1H), 7.42-7.36 (m, 2H), 7.29-7.25 (m, 1H), 4.27 (m, 2H), 1.88-1.82 (m, 2H), 1.33-1.26 (m, 6H), 0.88-0.85 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.6, 140.9, 140.5, 135.0, 131.9, 130.5, 129.7, 129.5, 126.4, 124.5, 123.0, 122.5, 120.6, 119.6, 112.4, 109.1, 108.9, 95.7, 87.2, 60.6, 43.3, 31.65, 29.8, 22.7, 14.4, 11.5.

2-cyano-3-(4-((9-hexyl-9H-carbazol-3-yl)ethynyl)phenyl)acrylic acid (CAPC Molecule):

A mixture of cyanoaceticacid (94 mg, 1.1 mmol), compound **6** (380 mg, 1.0 mmol) and a catalytic amount of piperidine were dissolved in acetonitrile 3 mL and refluxed for 10h. The orange red colored solid was separated out, filtered, washed excessively with acetonitrile and dried to give orange red powder. (304 mg, 68%). Mp 214-217 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 14.02 (bs, 1H), 8.48 (s, 1H), 8.36 (s, 1H), 8.25 (d, J = 8.75 Hz, 1H), 8.08 (d, J = 8.65 Hz, 2H), 7.75 (d, J = 10 Hz, 2H), 7.63- 7.65 (m, 3H), 7.52-7.49 (m, 1H) , 7.27-7.24 (m, 1H), 4.41 (t, J = 7.2 Hz, 2H), 1.78-1.73 (m, 2H), 1.29-1.20 (m, 6 H), 0.81-0.78 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 163.3, 153.2, 140.5, 140.1, 131.7, 131.0, 130.8, 129.2, 127.6, 126.5, 124.3, 122.3, 121.6, 120.8, 119.5, 116.2, 111.4, 109.9, 109.7, 103.7, 95.3, 87.4, 42.4, 30.9, 28.5, 26.1, 22.1, 13.9. HRMS (ESI): calculated = 446.1994; found [M + H^+] = 447.2059

Synthesis of PACC:

9-hexyl-6-iodo-9H-carbazole-3-carbaldehyde (7): The compound **2** (500 mg, 1.32 mmol) was dissolved in DMF (0.52 mL, 6.2 mmol) followed by addition of $POCl_3$ (0.223 mL, 2.25 mmol) at

0 ºC. The reaction mixture was allowed to come to room temperature and then heated at 90 C for 8 hours. Reaction mixture was poured in ice cold water and excess POCl3 was quenched with sodium bicarbonate. A light yellow oily product was obtained. The product was extracted with chloroform and purified by column chromatography on a silica gel column using hexane and ethyl acetate as the eluent [4 : 1 by vol.], to get a white solid product (360 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 8.49-8.41 (m, 2H), 8.01-7.99 (m, 1H), 7.75-7.73 (m, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.20 (d, J = 8.9 Hz, 1H), 4.26 (t, J = 7.3 Hz, 2H), 1.85-1.80 (m, 2H), 1.36-1.24 (m, 6H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.5, 143.8, 140.2, 134.9, 129.5, 128.8, 127.4, 125.3, 124.3, 121.6, 111.3, 109.17, 82.9, 43.5, 31.4, 28.8, 26.8, 22.4, 13.9.

9-hexyl-6-(phenylethynyl)-9H-carbazole-3-carbaldehyde (8):

A mixture of compound **7** (500 mg, 1.23 mmol), phenylacetylene (0.161 mL, 1.48 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 0.030 mmol), CuI (5 mg, 0.026 mmol) and Et_3N (0.362 ml) in tetrahydrofuran was stirred at 66 °C for 12 h under the nitrogen atmosphere. The mixture was cooled to room temperature to collect precipitates which were filtered to obtain crude product. The crude material was purified by column chromatography using hexane and ethyl acetate as the eluent [4 : 1 by vol,] to get the compound **8**. (245 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.00 (s, 1H), 8.33 (s, 1H), 8.12 (s, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.39 – 7.29 (m, 3H), 7.24 (d, J = 8.9 Hz, 1H), 7.18 (d, J = 8.9 Hz, 1H), 4.02 (t, J = 7.2 Hz, 2H), 1.75 – 1.60 (m, 2H), 1.33 – 1.12 (m, 6H), 0.83 (t, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.0, 144.7, 144.1, 131.1, 129.7, 128.4, 128.1, 127.6, 126.7, 123.6, 123.3, 122.3, 121.9, 114.3, 108.9, 108.7, 90.1, 88.0, 42.8, 31.0, 28.4, 26.4, 22.1, 13.7.

2-cyano-3-(9-hexyl-6-(phenylethynyl)-9H-carbazol-3-yl) acrylic acid (PACC Molecule): A mixture of cyanoaceticacid (94 mg, 1.1 mmol), compound **8** (380 mg, 1.0 mmol) and a catalytic amount of ammonium acetate were dissolved in acetic acid 3 mL and refluxed for 10h. The greenish colored solid separated out, washed with acetic acid, filtered and dried under vacuum. (275 mg, 61%). Mp 205-208 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): δ 13.74 (bs, 1H), 8.85 (s, 1H), 8.43 (s, 1H), 8.36 (s, 1H), 8.31 (d, J = 10.7 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.73-7.68 (m, 2H), 7.61-7.60 (m, 2H), 7.46-7.41 (m, 3H), 4.44-4.42 (m, 2H), 1.79-1.73 (m, 2H), 1.26-1.19 (m, 6H), 0.78 (t, J = 7.05 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.1, 155.0, 143.1, 140.4, 131.2, 130.1, 128.8, 128.4, 128.1, 125.9, 123.8, 122.9, 122.8, 122.1, 122.0, 117.2, 113.8, 110.7, 110.6, 98.9, 90.3, 88.2, 42.8, 30.9, 28.5, 26.0, 22.0, 13.8. HRMS (ESI): calculated = 446.1994; found [M + H$^+$] = 447.2061.

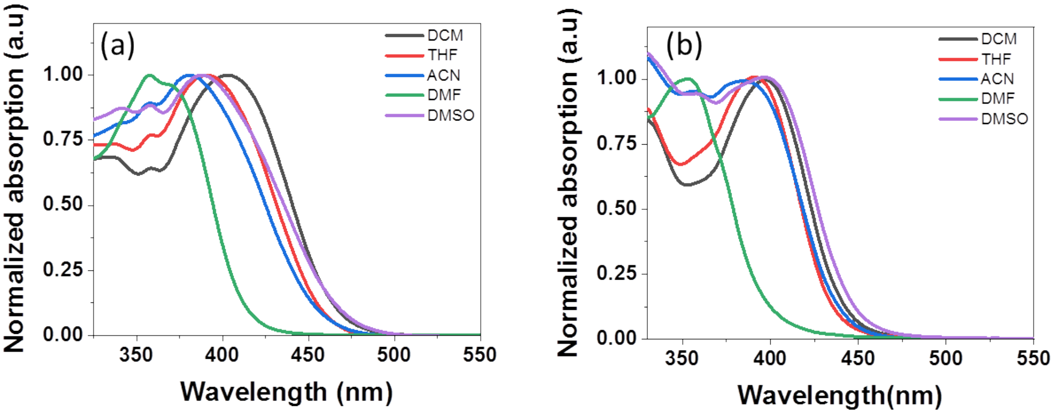

Fig. S1 UV-vis absorption spectra of the synthesized compounds (a) **CAPC** and (b) **PACC** in different solvents (concentration 5 µM).

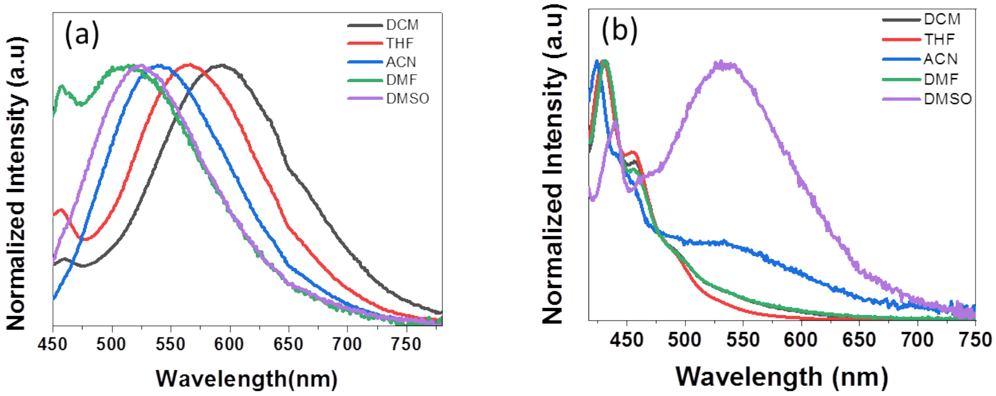

Fig. S2 PL spectra of the synthesized compounds (a) **CAPC** and (b) **PACC** in different solvents (concentration 5 µM).

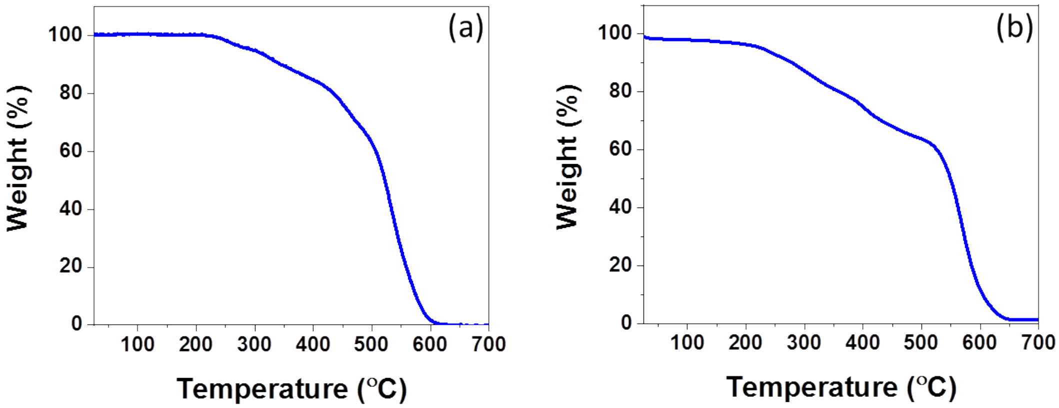

Fig. S3 Thermal Gravimetric analysis data recorded at a heating rate of 10 °C min^{-1} of (a) **CAPC** and (b) **PACC**

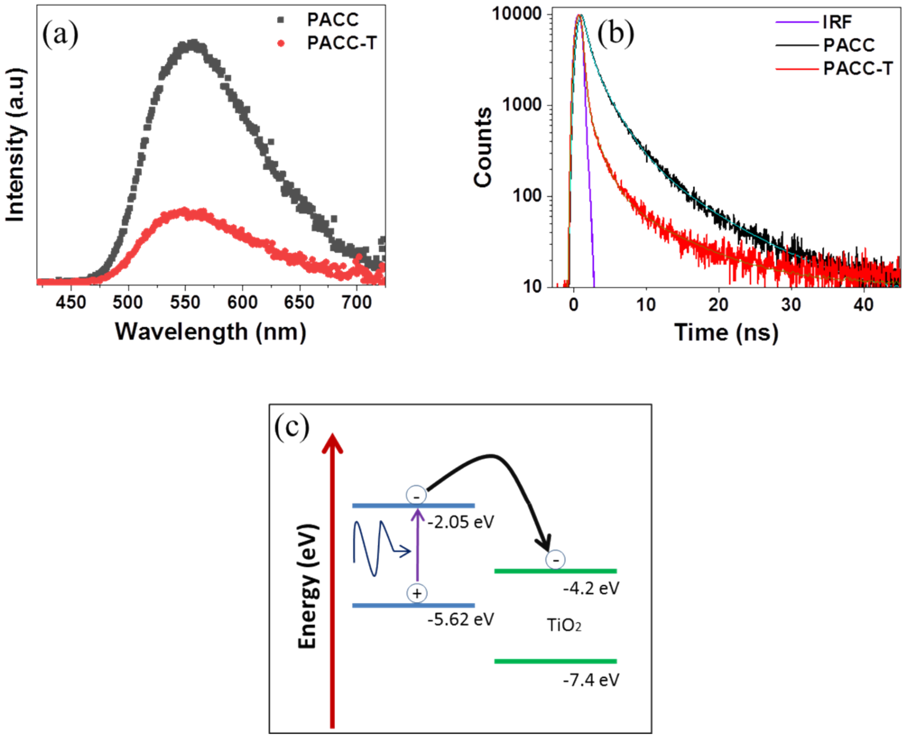

Fig. S4 (a) Fluorescence quenching of **PACC** dye in the presence of TiO_2 NP layer. (b) Fluorescence decays of **PACC** dye film and **PACC** dye-TiO_2 film (**PACC-T**) recorded using TCSPC. (c) Schematic representation of energy levels of **PACC** molecule and TiO_2 NPs showing possibility of electron transfer from photoexcited dye.

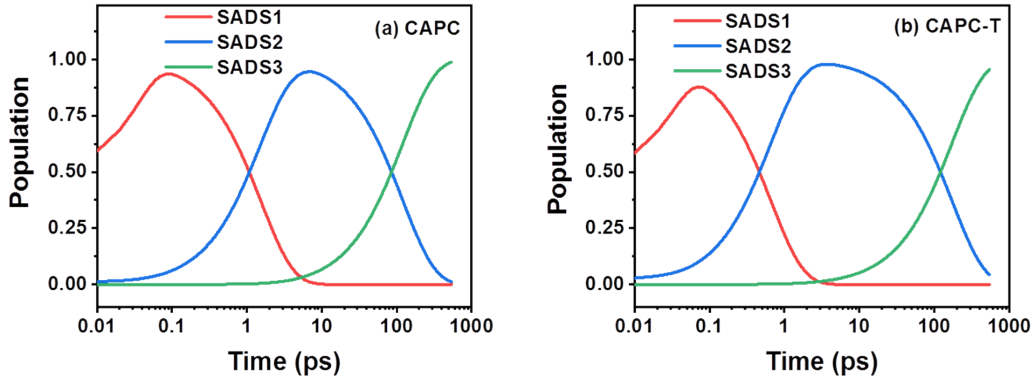

Fig. S5 The population profiles of estimated SADSs arising out of global fitting of TA data: (a) **CAPC** dye film and (b) CAPC-TiO_2 NP (**CAPC-T**) film.

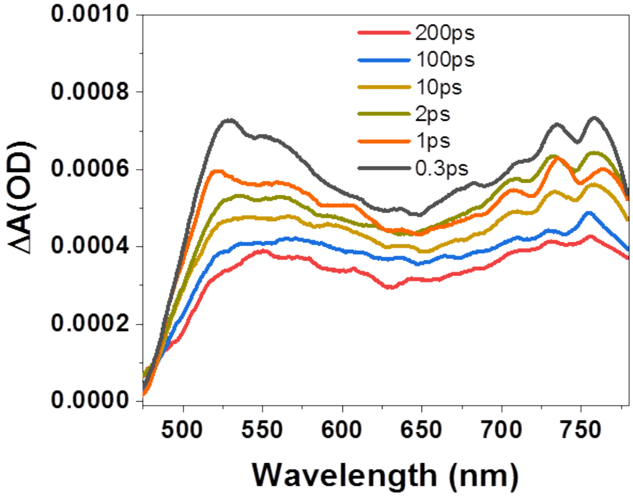

Fig. S6 TA spectra of CAPC-TiO$_2$ NPs (**CAPC-T**) film excited at 360 nm with a pump energy 400 μJ/cm^2/pulse.

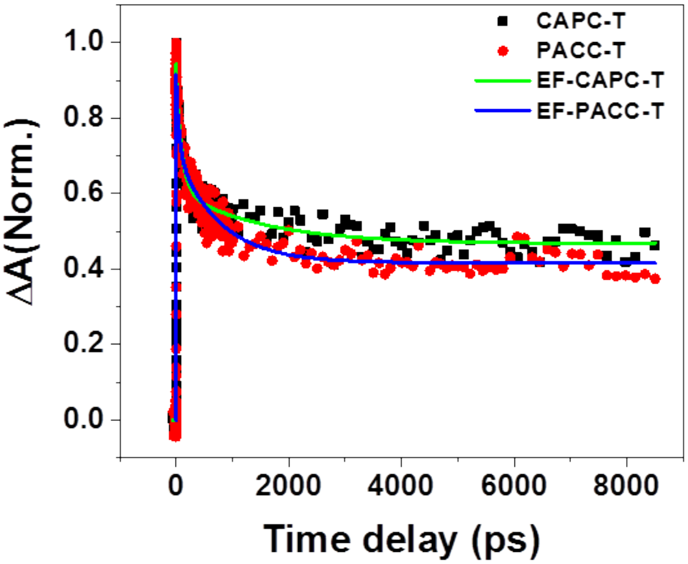

Fig. S7 TA Kinetics at 725 nm for CAPC-TiO$_2$ NPs (**CAPC-T**) film and PACC-TiO$_2$ NPs (**PACC-T**) film excited at 360 nm with a pump energy 400 μJ/cm^2/pulse.

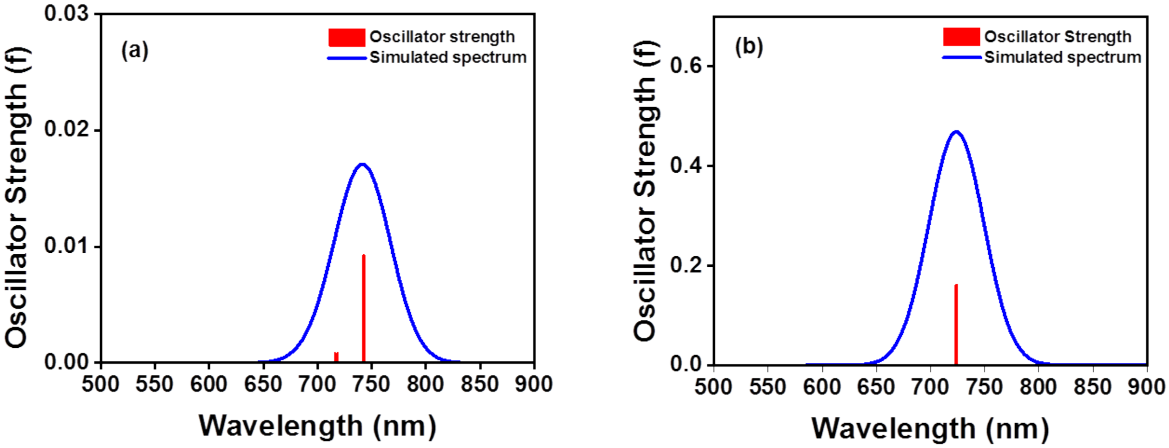

Fig. S8 Simulated absorption spectra of dye cation of (a) CAPC and (b) PACC.

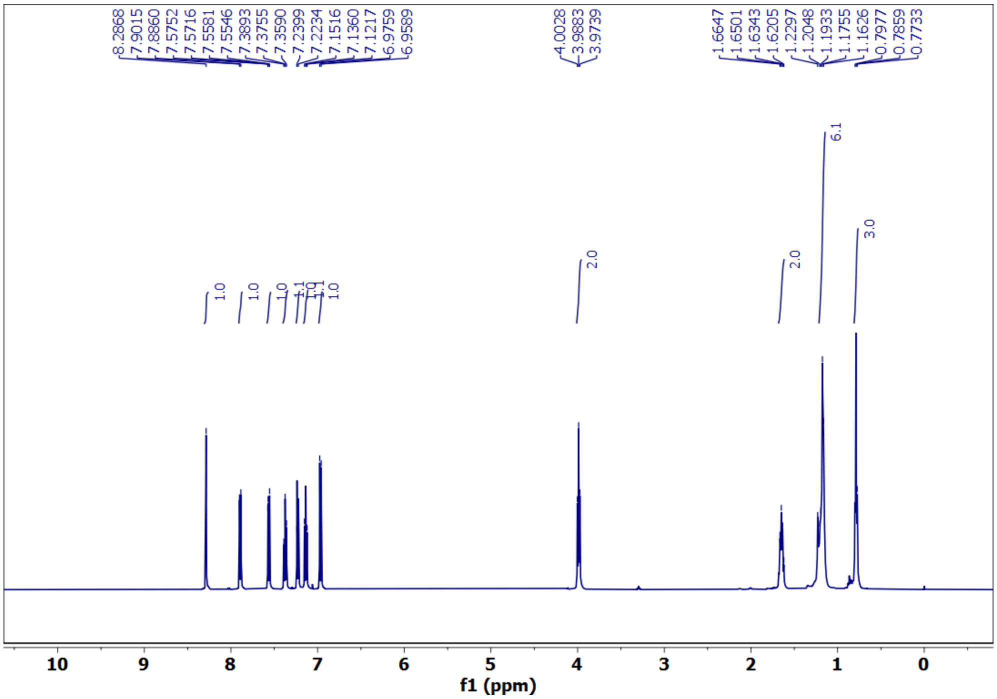

Fig. S9 ^{1}H NMR spectrum of compound 2

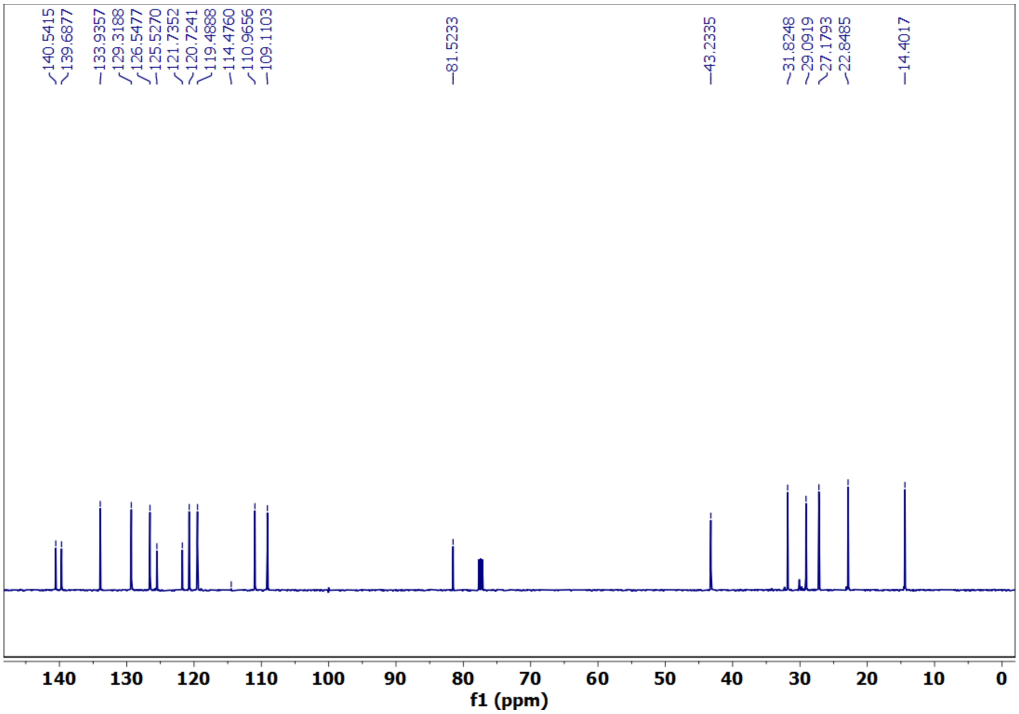

Fig. S10 ^{13}C NMR spectrum of compound 2

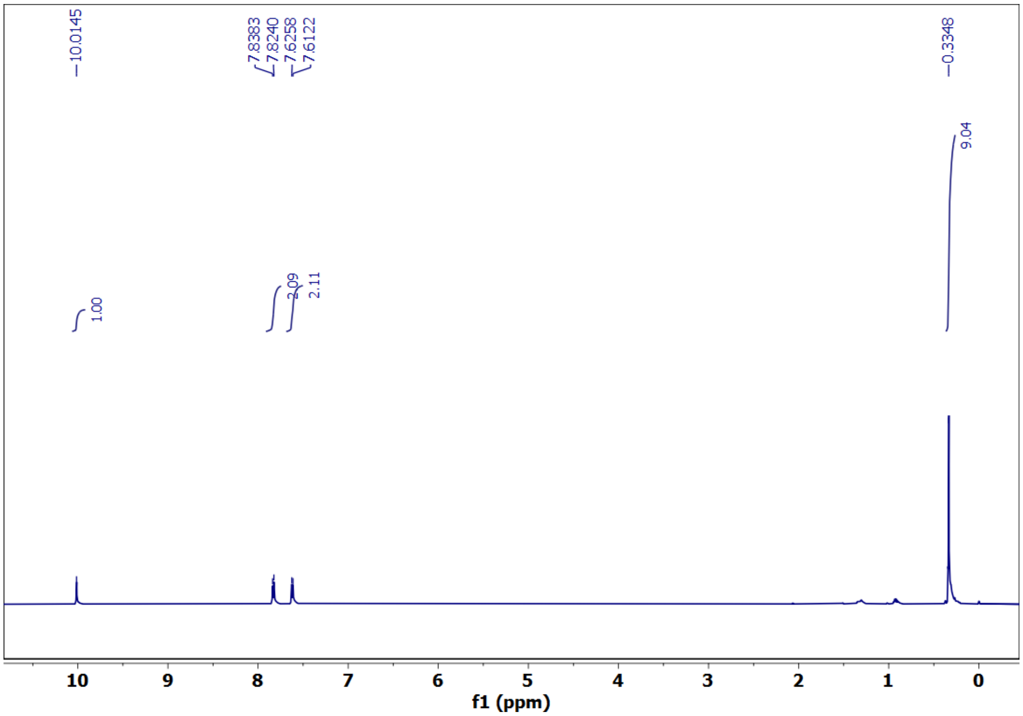

Fig. S11 ^{1}H NMR spectrum of compound 4

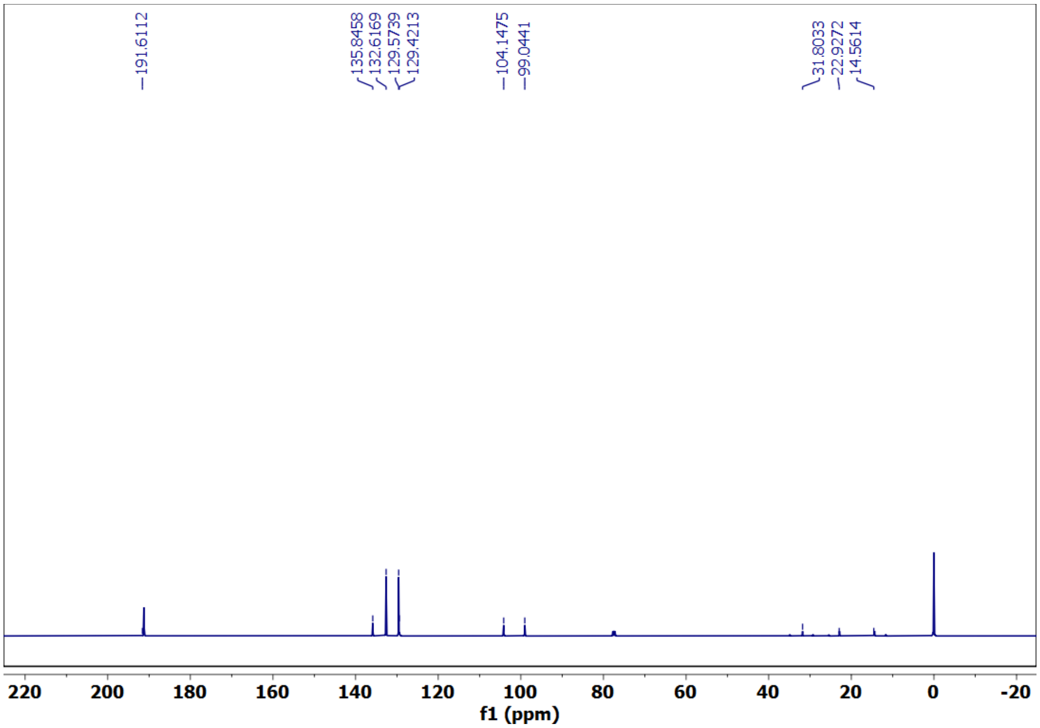

Fig. S12 ^{13}C NMR spectrum of compound 4

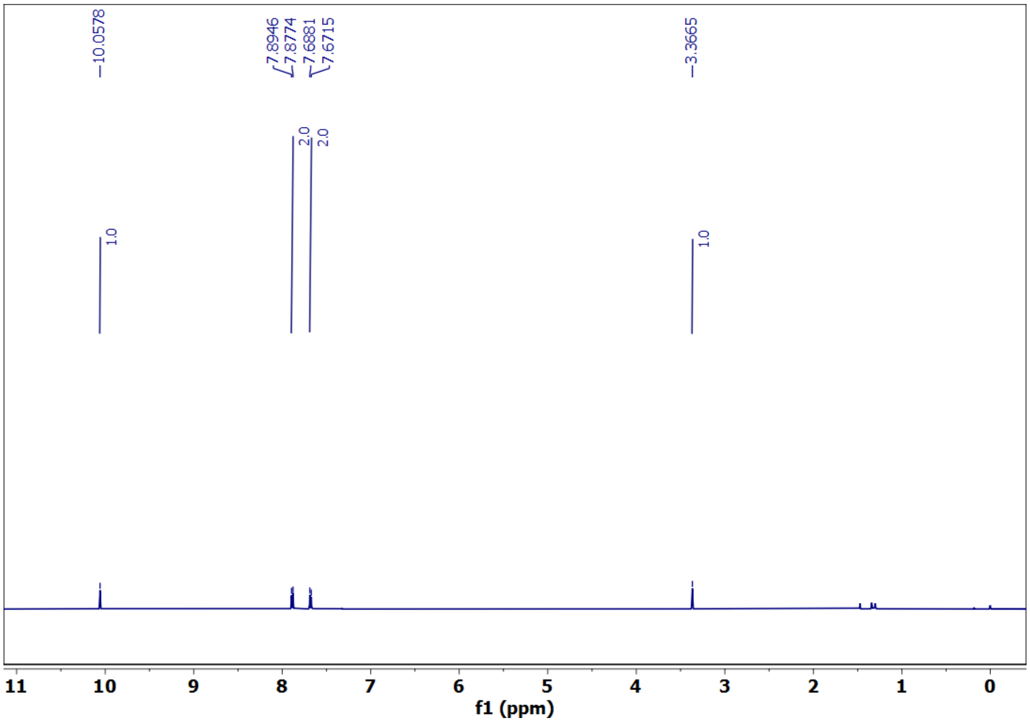

Fig. S13 ^{1}H NMR spectrum of compound 5

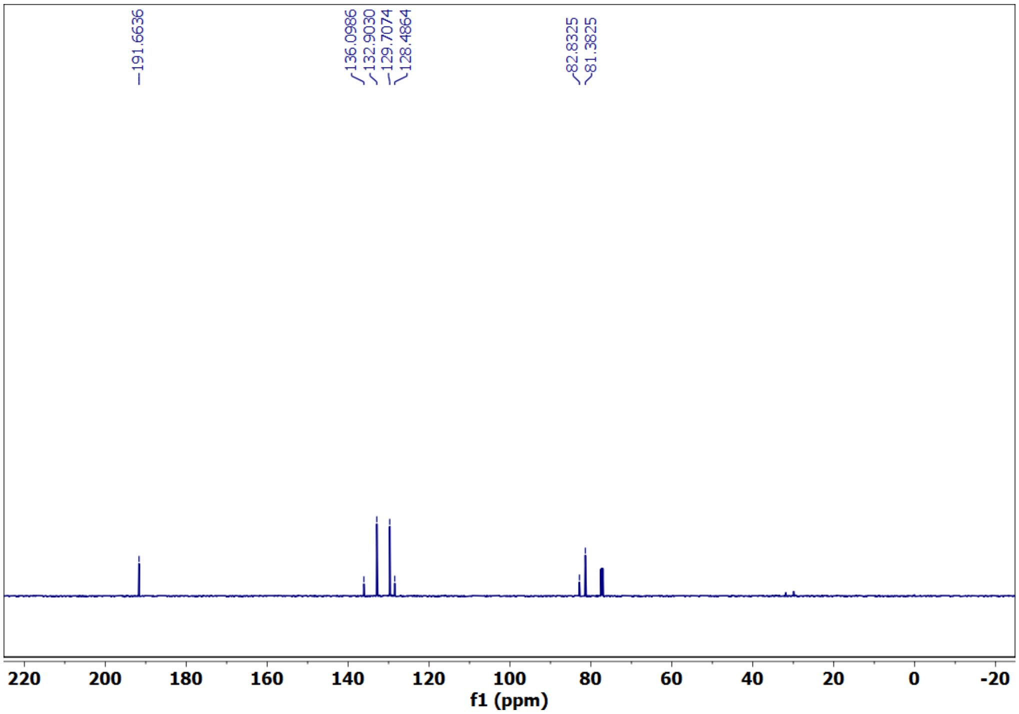

Fig. S14 ^{13}C NMR spectrum of compound 5

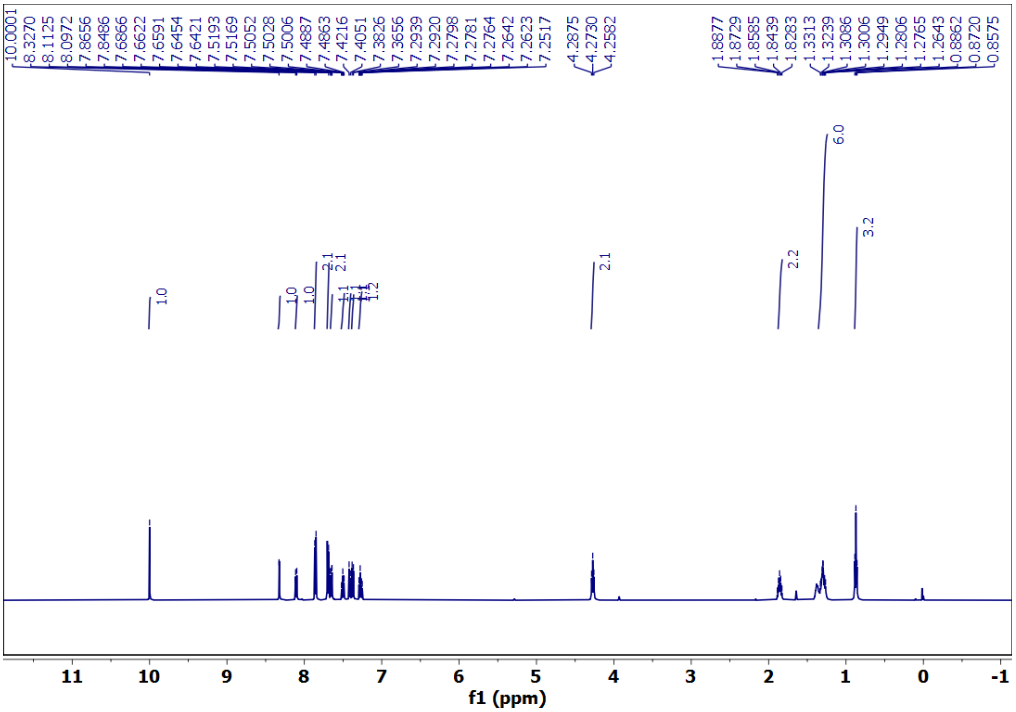

Fig. S15 ^{1}H NMR spectrum of compound 6

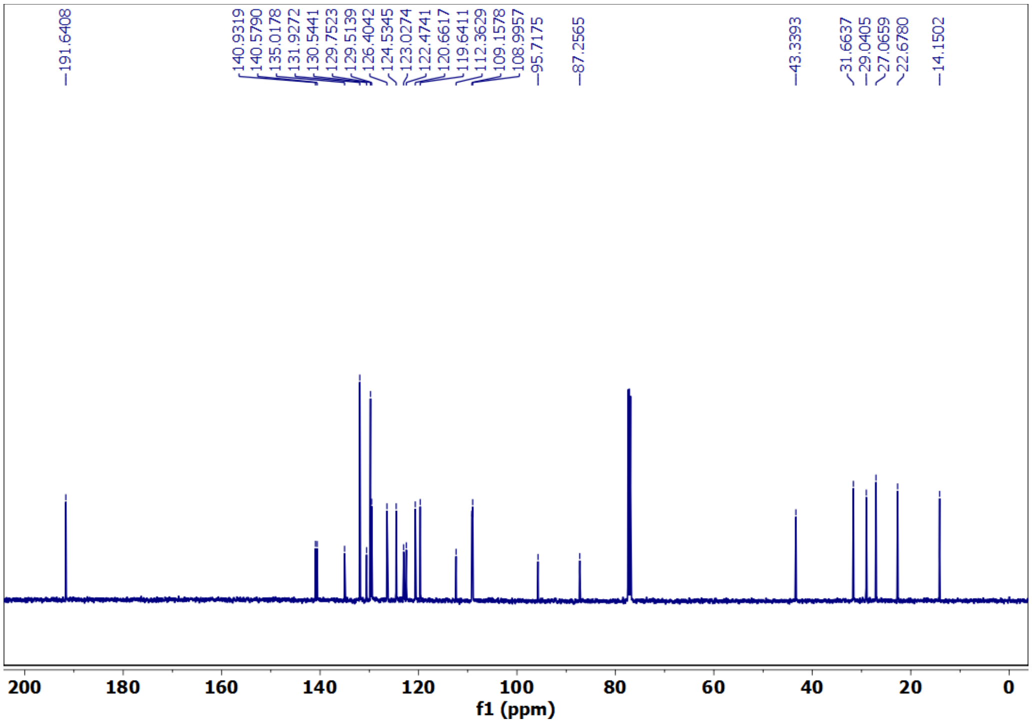

Fig. S16 ^{13}C NMR spectrum of compound 6

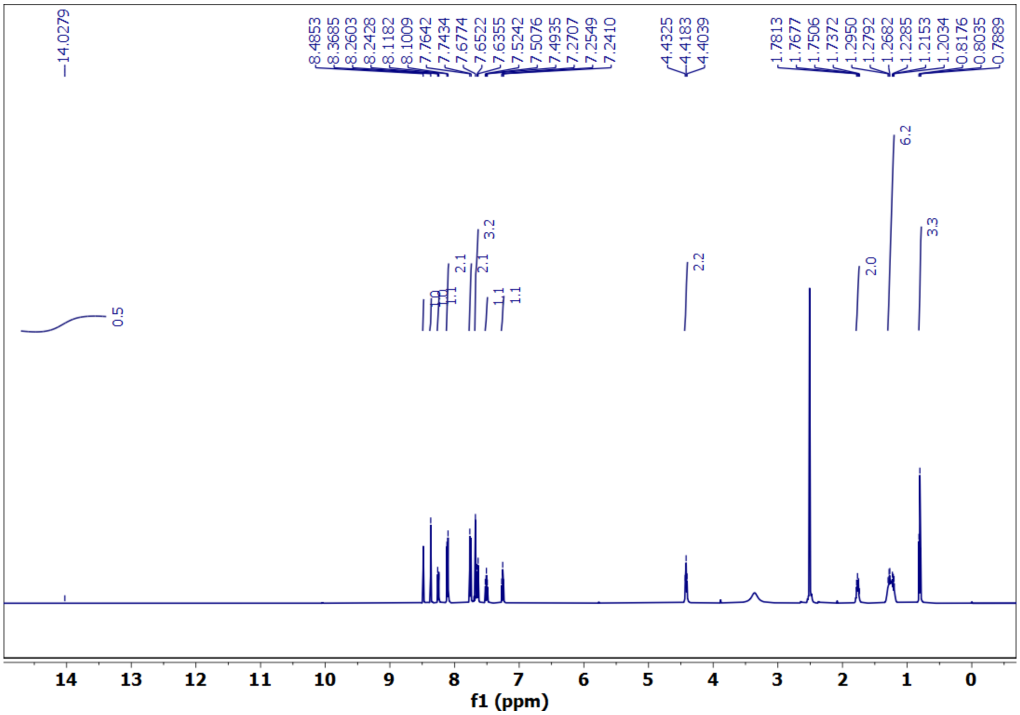

Fig. S17 ^{1}H NMR spectrum of compound CAPC

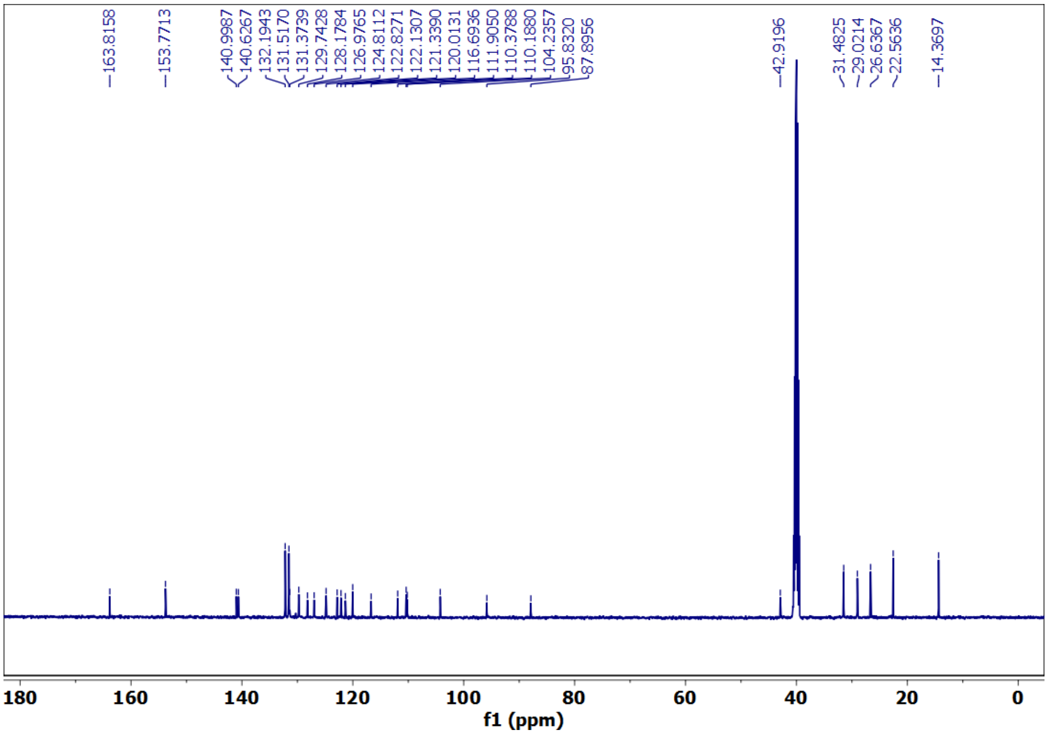

Fig. S18 ^{13}C NMR spectrum of compound CAPC

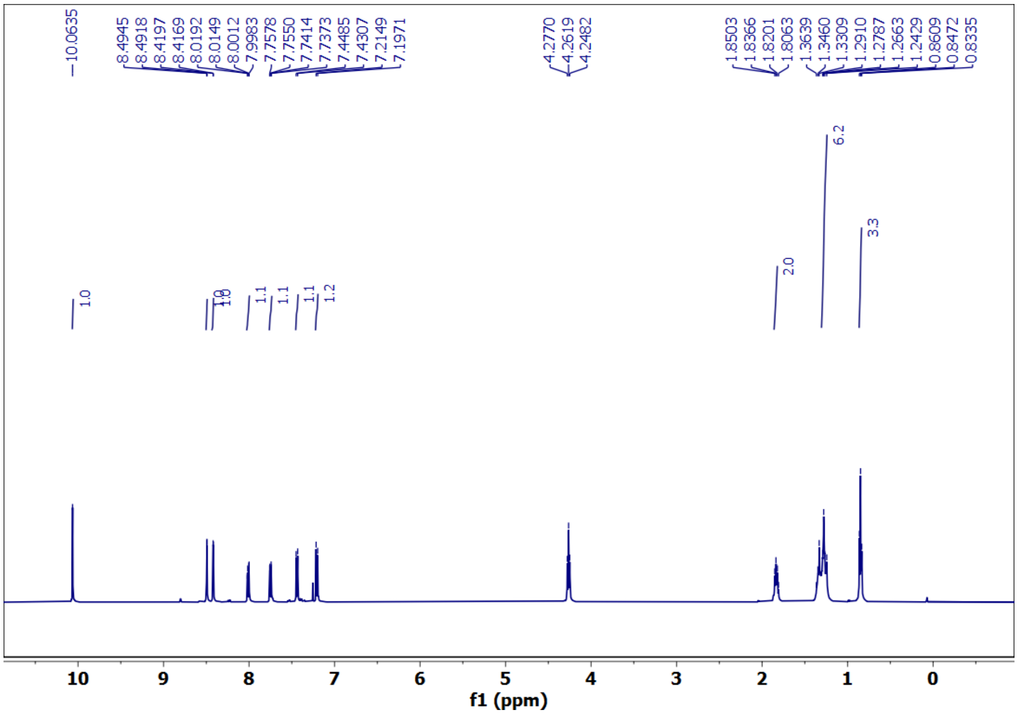

Fig. S19 ^{1}H NMR spectrum of compound 7

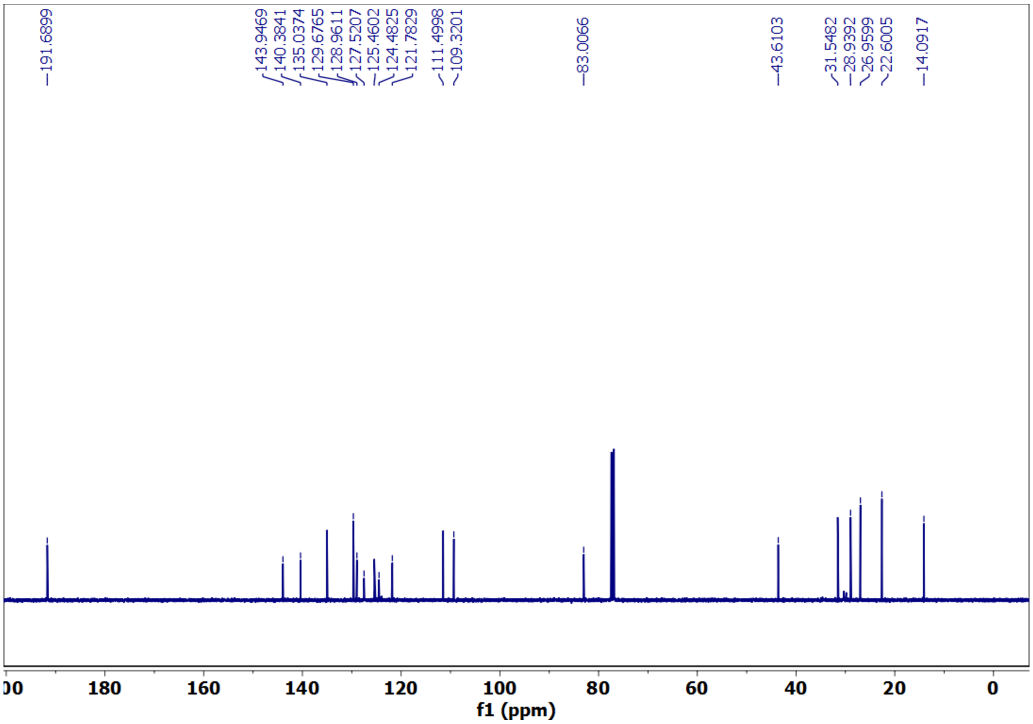

Fig. S20 ^{13}C NMR spectrum of compound 7

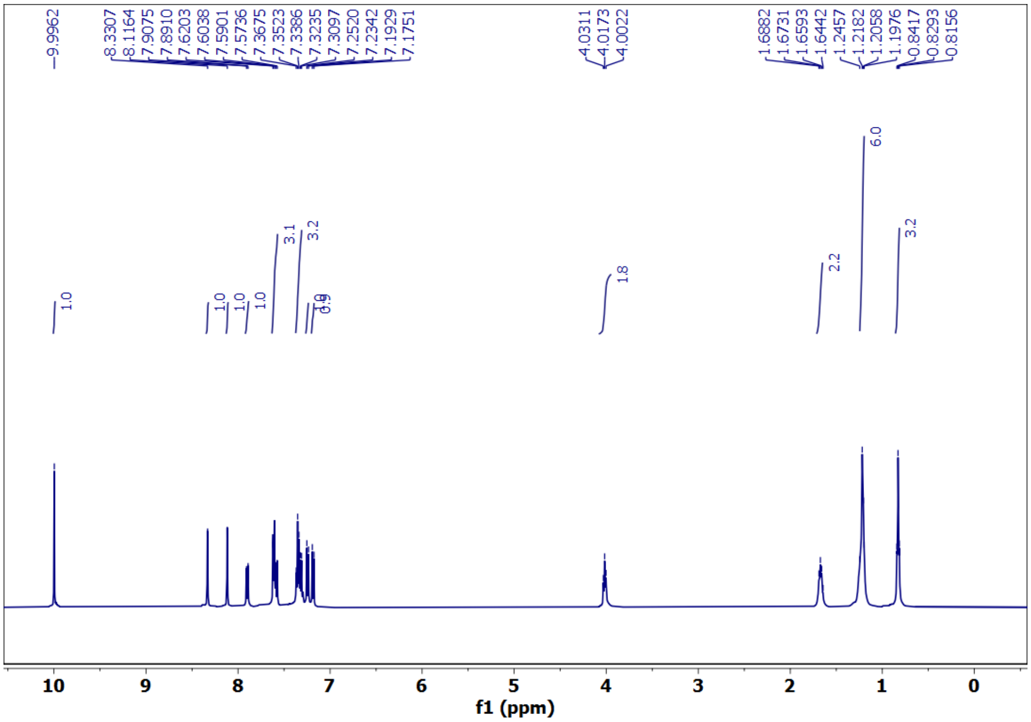

Fig. S21 ^{1}H NMR spectrum of compound 8

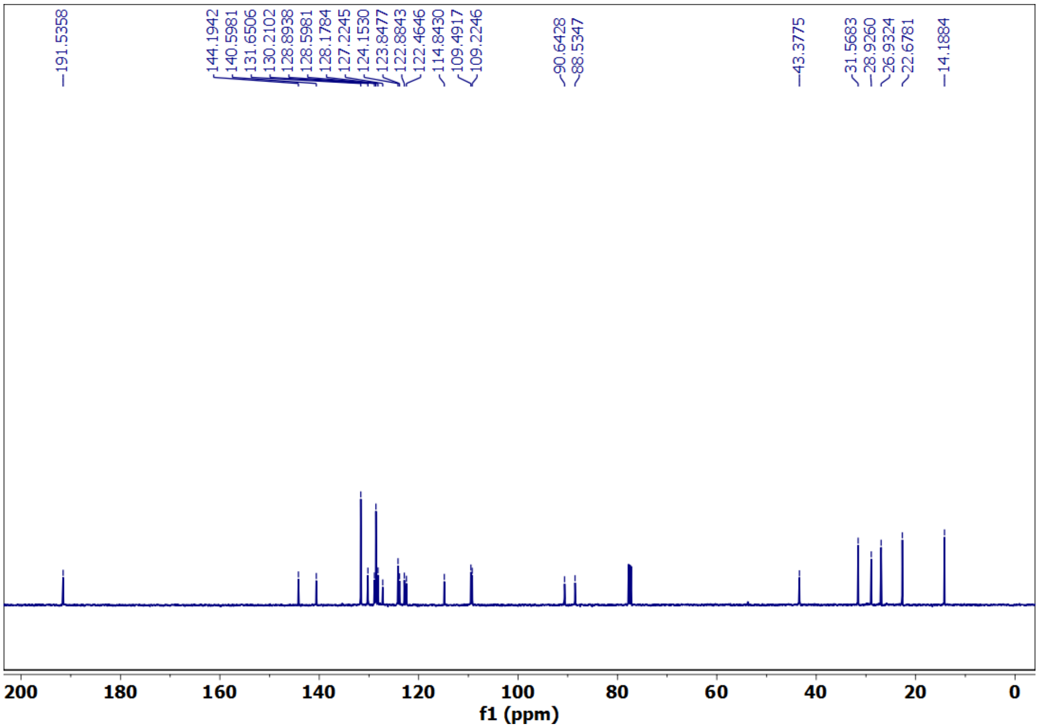

Fig. S22 ^{13}C NMR spectrum of compound 8

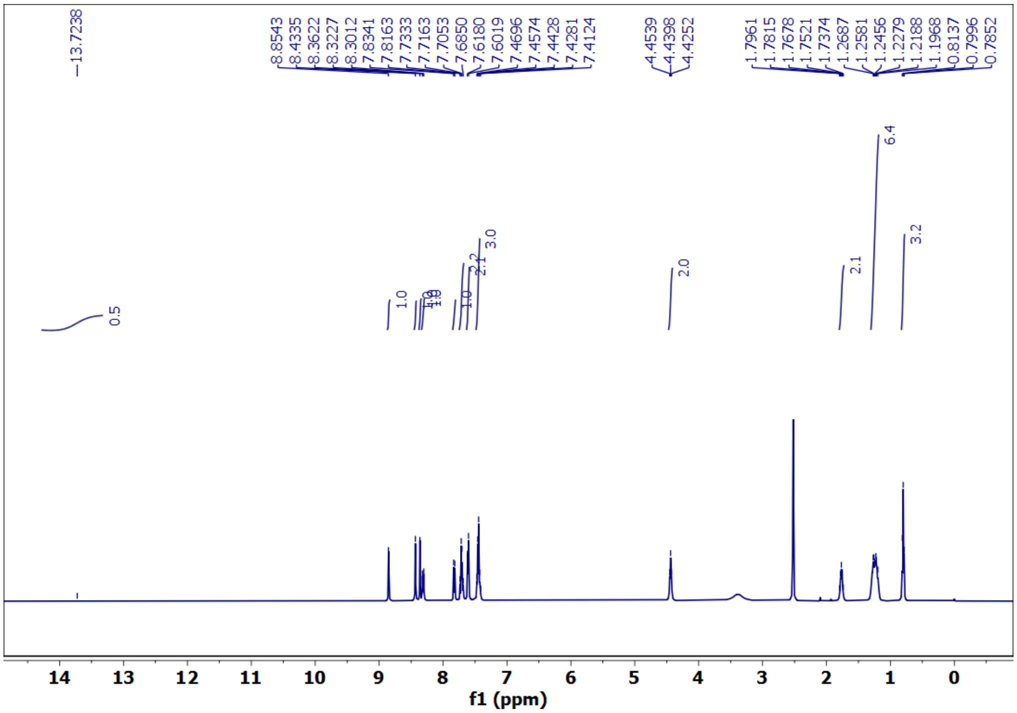

Fig. S23 ^{1}H NMR spectrum of compound PACC

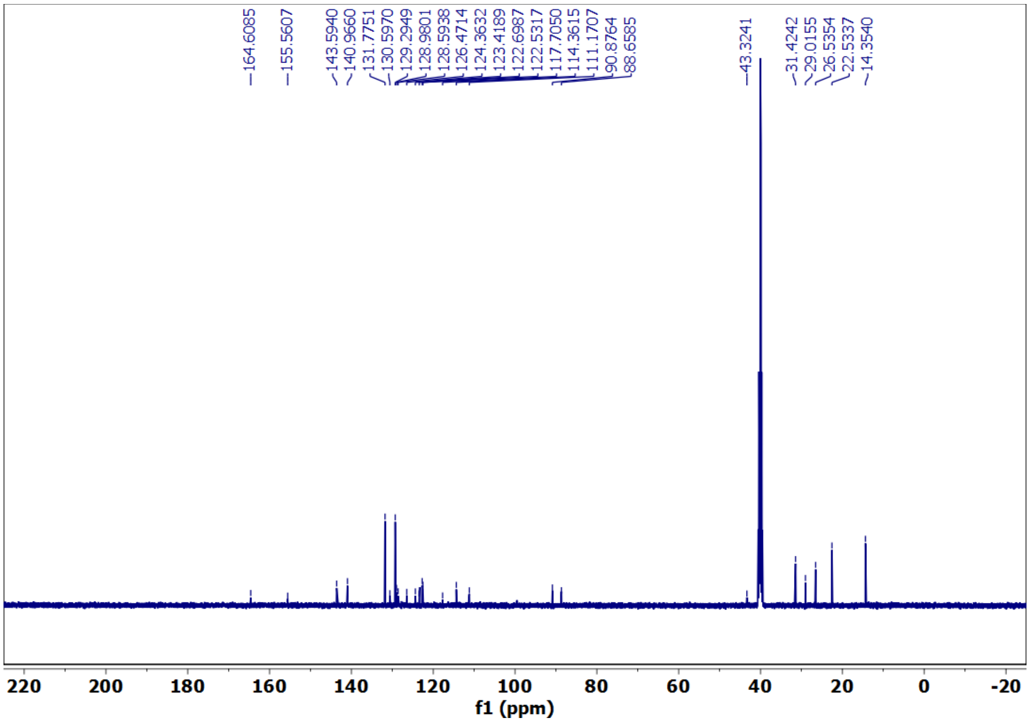

Fig. S24 ^{13}C NMR spectrum of compound PACC

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