Electronic Supporting Information

Synthesis and Photovoltaic Application of NIR-emitting Perylene-monoimide Dyes with Large Stokes-shift

Vikas Sharma,[a‡] Kovida,[a‡] Dhananjaya Sahoo,[a] Nonu Varghese,[b] Kallol Mohanta*[b] and Apurba Lal Koner*[a]

[a] Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462 066, Madhya Pradesh, India, E-mail: akoner@iiserb.ac.in

[b] Department of Physics, PSG College of Technology & PSG Institute of Advanced Studies, Peelamedu, Avinashi Road, Coimbatore - 641004,Tamilnadu, India.

‡ these authors contributed equally to this work

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(A) General Proceduce:

(a) Chemicals:

All the solvents and reagents were purchased from commercial sources and were used as received. Perylene-3,4,9,10-tetracarboxylic dianhydride, Ethylhexylamine, 4-Ethynyl-N,N-dimethylaniline, Dichlorobis(triphenylphosphine)palladium(II), (Triisopropylsilyl)acetylene and CuI were purchased from Sigma Aldrich. $Zn(OAc)_2.2H_2O$ and liquid Br_2 were purchased from Merck. Molten imidazole was purchased from Spectrochem. Tetrakis(triphenylphosphine)palladium(0) and *p*-tolylacetylene was purchased from TCI. For coupling reactions, THF, TEA and DIPEA were purchased from Ranchem, Spectrochem and Sigma Aldrich respectively.

(b) Steady State Measurements:

All the spectroscopic grade solvents like Acetonitrile, DCM, DMSO, EtOH, THF, Toluene, Dioxane, $CHCl_3$ were purchased from SRL, DMF was purchased from Sigma. The stock solutions of 1 mM concentration of dye were made in Toluene. The concentration of dyes was kept 5 μM for all the measurements. All steady-state absorption and fluorescence measurements were carried out using Cary 5000 UV-spectrophotometer from Agilent Technologies using 1 cm path length quartz cuvettes. All solvent dependent steady-state fluorescence measurements were carried out using HORIBA Jobin Yvon Fluorolog fluorimeter using Origin 8.0 software provided with the instrument. Fluorescence spectra were recorded using 1 cm path length quartz cuvette and keeping both excitation and emission slit at 2 nm with very dilute solutions having OD less than 0.1 at excitation wavelength. All the experiments were carried out at ambient temperature (298 K) as otherwise mentioned.

(c) Fluorescence Lifetime Measurement Using Time Resolved Single Photon Counting

Time-resolved fluorescence measurements were performed using a Hamamatsu MCP photomultiplier (R-3809U-50). All the measurements were carried out at ambient temperature (298 K) using a very dilute solution with OD less than 0.1. The concentration of dyes was kept at 5 μM.

(d) Electrochemical Measurements:

Electrochemical measurements were carried out using a CHI 6205 electrochemical analyzer using tetra-*n*-butylammoniumhexafluoro-phosphate as the supporting electrolyte (0.1 M) and the dye concentration was *ca*. 10^{-3} M. For a tpical electrochemical measurement a glassy carbon as working electrode, Pt wire as counter electrode and aqueous saturated Ag/AgCl as reference electrode were used. In this cell, all the voltammogram were measured at 0.1 V/s scan rate in dichloromethane. The dye solution in dichloromethane was purged with nitrogen for 15 minutes to remove dissolved oxygen. Every time before measurement the electrode was polished on a felt pad with alumina and washed thoroughly. All the measurements were repeated at least three times for reproducibility.

(e) Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry:

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker spectrometer in $CDCl_3$ solvent. Chemical shifts were reported in ppm scale with respect to the residual solvent signal at δ= 7.26 in $CDCl_3$ for ^{1}H NMR at 500 MHz. The mass spectra for all the compounds were recorded using APCI with solutions of dyes in Chloroform.

(f) Density Functional Theory (DFT) Calculations:

The theoretical calculations to obtain HOMO-LUMO profiles of all the compounds were done using Biovia Materials Studio version 2017 with B3LYP as the functional and DNP (double numerical polarized) as the basis set.

(g) **Photovoltaic Device fabrication:** The PMI-$(NMe_2)_4$ molecule was blended with the [6,6]-Phenyl C61 butyric acid methyl ester ($PC_{61}BM$) at 1:4 ratio and the concentration was maintained as 5 mg/ml in 1,2-dichlorobenzene. The mixture was then spin-coated on the top of cleaned ITO substrates. The spin-coating condition was 1500 rpm for 60 sec. A short drying period of 30 min at 80 °C was carried out before the 300 nm Al electrode was deposited over the thin film.

(B) Synthesis:

(a) Synthesis of PMI-$(NMe_2)_4$ (2a): Tetrabromo PMI (100 mg, 0.1334 mmol), 4-Ethynyl-N,N-dimethylaniline (116.3 mg, 0.8009 mmol) were taken in a Schlenk tube. To this, dry THF (1 mL), N, N-Diisopropylethylamine (1 mL) were added and the mixture was stirred for 5 minutes at room temperature. The resulting solution was degassed thrice by freeze pump thaw cycles. Then $Pd(PPh_3)_4$ (28.2 mg, 0.0244 mmol) and CuI (25.2 mg, 0.1321 mmol) were added to the Schlenk tube under N_2 atmosphere. The reaction mixture was evacuated and flushed with N_2 twice followed by heating at 80 °C for 15 h. After that it was cooled to room temperature. Solvent was evaporated using rotary evaporator and the residue was purified by column chromatography (Neural alumina, 2:1 DCM-Hexane eluent) providing the desired compound (45 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.85 (d, J = 8.2 Hz, 2H), 8.79 (s, 2H), 7.99 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.9 Hz, 4H), 7.36 (d, J = 8.9 Hz, 4H), 6.74 (d, J = 8.9 Hz, 4H), 6.53 (d, J = 8.9 Hz, 4H), 4.17 (m, 2H), 3.05 (s, 12H), 2.98 (s, 12H), 1.98 (m, 1H), 1.39 (m, 8H), 0.96 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.03, 150.57, 150.20, 137.35, 135.71, 133.51, 133.34, 133.12, 128.42, 127.34, 125.01, 119.60, 118.88, 112.10, 111.79, 110.96, 109.82, 102.47, 97.42, 90.48, 89.75, 40.37, 40.33, 38.09, 31.00, 28.96, 24.29, 23.24, 14.30, 10.84.

APCI-HRMS (1006.5067 g/mol calcd. for $C_{70}H_{63}N_5O_2$): m/z 1006.4982 [M+H]

IR: frequency/ cm^{-1}: 2950 (CH, m), 2180 (C≡C, w), 1680 (C=O, s), 1665 (C=C, w), 1350 (C-N, s) and 1130 (C-N, m), 710 (CH bending, s) and 860 (C=C bending, m)

(b) Synthesis of PMI-$(MeO)_4$ (2b): TetrabromoPMI (40 mg, 0.053 mmol), 4-Ethynylanisole (38 μL, 0.293 mmol) were taken in a Schlenk tube. To this, dry THF (1 mL), triethylamine (1 mL) were added and the mixture was stirred for 5 minutes at room temperature. The resulting solution was degassed thrice by freeze pump thaw cycles. Then $PdCl_2(PPh_3)_2$ (3.86 mg, 0.0055 mmol) and CuI (6.47 mg, 0.034 mmol) were added to the Schlenk tube under N_2 atmosphere. The reaction mixture was evacuated and flushed with N_2 twice followed by heating at 60°C for 12 h. After that it was cooled to room temperature. Solvent was evaporated using rotary evaporator and the residue was purified by column chromatography (Silica, 1:1 DCM-Hexane eluent) affording the desired compound (60%) yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.74 (d, *J* = 8.2 Hz, 2H), 8.75 (s, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 4H), 7.36 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 6.71 (d, *J* = 8.8 Hz, 4H), 4.15 (m, 2H), 3.87 (s, 6H), 3.80 (s, 6H), 1.96 (m, 1H), 1.38 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 163.51, 160.29, 159.81, 137.47, 135.67, 133.80, 133.49, 133.38, 128.46, 127.27, 124.32, 119.76, 118.40, 115.93, 115.13, 114.41, 113.82, 100.73, 96.20, 90.58, 89.70, 55.49, 55.43, 44.20, 38.06, 30.99, 28.92, 24.26, 23.23, 14.29, 10.78.

APCI-HRMS (954.3789 g/mol calcd for $C_{66}H_{51}NO_6$): m/z 954.3716 [M+H]

IR: frequency/ cm^{-1}: 2950 (C-H, m), 2180 (C≡C, w), 1680 (C=O, s), 1670 (C=C, m), 1250 (C-O, s), 1150 (C-N, m), 1110 (C-C, m), 820 (C=C bending, m)

(c) Synthesis of PMI-(TIPS)$_4$ (2c): TetrabromoPMI (40 mg, 0.053 mmol), (Triisopropylsilyl)acetylene (69 μL, 0.293 mmol) were taken in a Schlenk tube. To this, dry THF (1 mL), triethylamine (1 mL) were added and the mixture was stirred for 5 minutes at room temperature. The resulting solution was degassed thrice by freeze pump thaw cycles. Then $PdCl_2(PPh_3)_2$ (3.86 mg, 0.0055 mmol) and CuI (6.47 mg, 0.034 mmol) were added to the Schlenk tube under N_2 atmosphere. The reaction mixture was evacuated and flushed with N_2 twice followed by heating at 60°C for 18 h. After that it was cooled to room temperature. Solvent was evaporated using rotary evaporator and the residue was purified by column chromatography (Silica, 1:1 DCM:Hexane eluent) affording the desired compound (72% yield).

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.89 (d, *J* = 8.2 Hz, 2H), 8.76 (s, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 4.14 (m, 2H), 1.99 – 1.90 (m, 1H), 1.37 (m, 8H), 1.20 (dd, *J* = 8.3, 3.3 Hz, 71H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): *δ* 163.76, 139.02, 137.19, 136.93, 129.93, 129.42, 128.51, 128.07, 127.32, 124.84, 120.10, 118.61, 108.41, 108.17, 106.89, 99.80, 44.49, 38.15, 31.02, 29.00, 24.28, 19.17, 18.94, 14.27, 12.09, 11.58, 10.82.

APCI-HRMS (1154.7431 g/mol calcd for $C_{39}H_{33}NO_2$): m/z 1154.7379 [M+H]

IR: frequency/ cm^{-1}: 2950 (C-H, s), 2250 (C≡C, w), 1680 (C=O, m), 1660 (C=C, w), 1250 (C-N, m), 810 (C=C bending, s), 700 (C-H bending, s)

Table S1: Solvent-dependent photophysical properties

Compound	Solvents	$\varepsilon \times 10^4$/ $(M^{-1}cm^{-1})$ (λ_{max}^{Abs}/nm)	λ_{max}^{Em} (nm)	□□ (cm^{-1})^{a}	τ_{avg} (ns)
2a	$CHCl_3$	8.09, (665)	869	3530	1.0
	DCM	7.60, (667)	879	3616	0.4
	Dioxane	5.31, (653)	838	3381	1.6
	THF	8.31, (666)	880	3651	0.2
	Toluene	8.44, (665)	879	3661	2.2
	ACN	2.85 (615)	847	4454	nd
2b	$CHCl_3$	7.72, (618)	688	1646	3.3
	DCM	7.24, (612)	688	1805	3.2
	Dioxane	8.66, (606)	658	1304	4.2
	DMF	8.50, (610)	701	2128	2.5
	THF	8.62, (610)	675	1578	3.4
	Toluene	8.92, (614)	659	1112	4.3
2c	$CHCl_3$	4.74, (580)	627	1292	5.1
	DCM	4.42, (577)	625	1331	5.2
	Dioxane	5.62, (570)	607	1069	5.5
	DMF	5.72, (569)	626	1601	5.0
	THF	5.68, (569)	612	1235	5.4
	Toluene	5.84, (575)	606	889	5.5

[a] Stokes shift (SS), $\bar{\nu}_a - \bar{\nu}_f$, nd- not determined

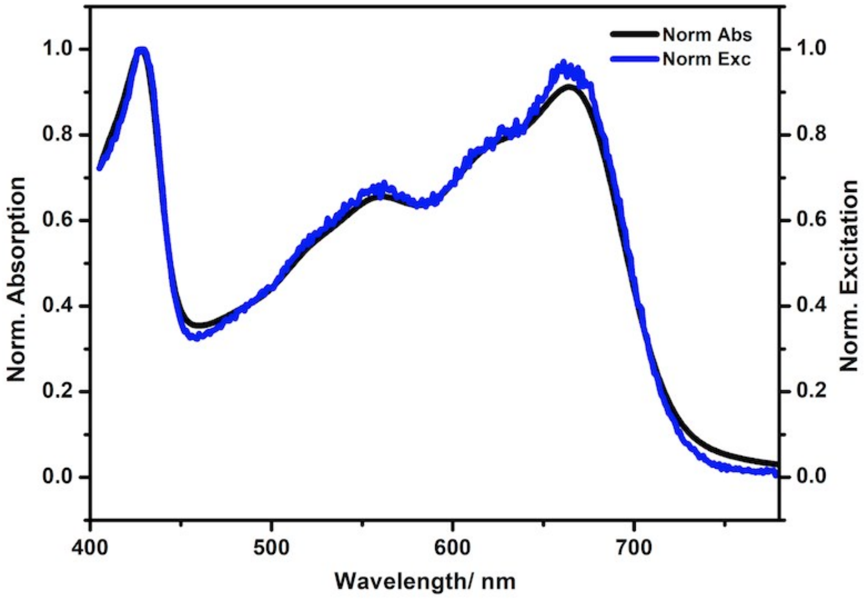


Fig. S1: Verification of optical purity by matching UV-Vis. and excitation spectra of **2a** in Toluene

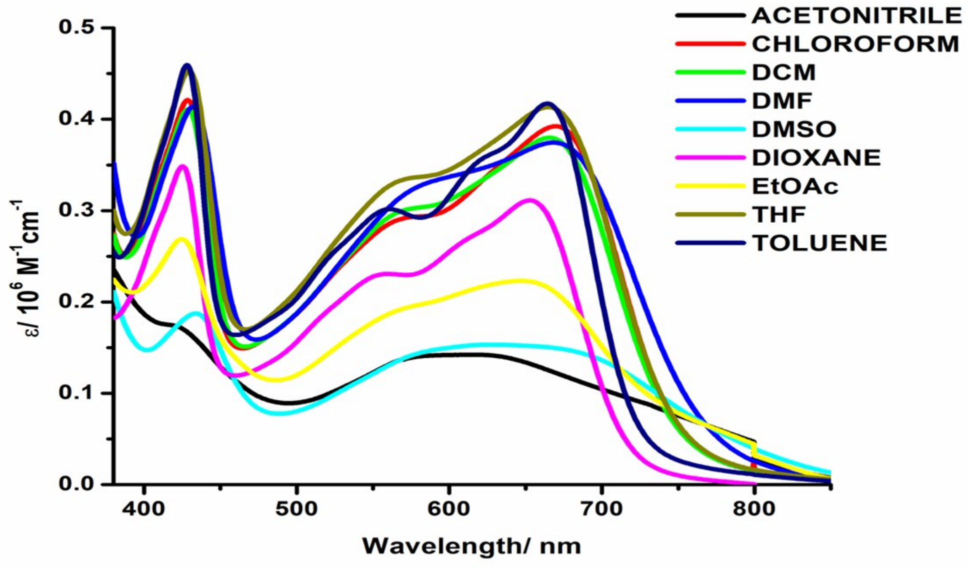


Fig. S2: Solvent-dependent UV-Vis. Spectra of **2a** at 5 μM concentration

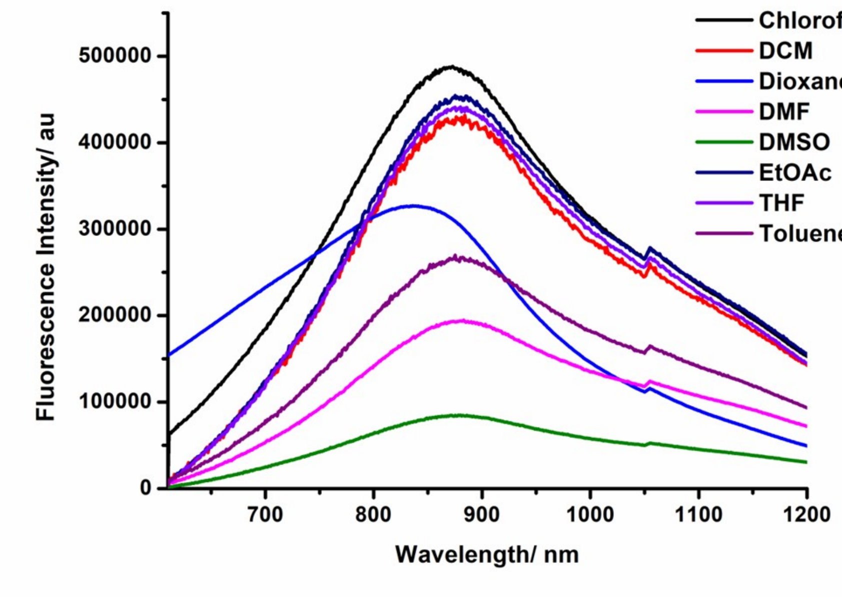


Fig. S3: Solvent-dependent fluorescence spectra of **2a** at 5 μM concentration

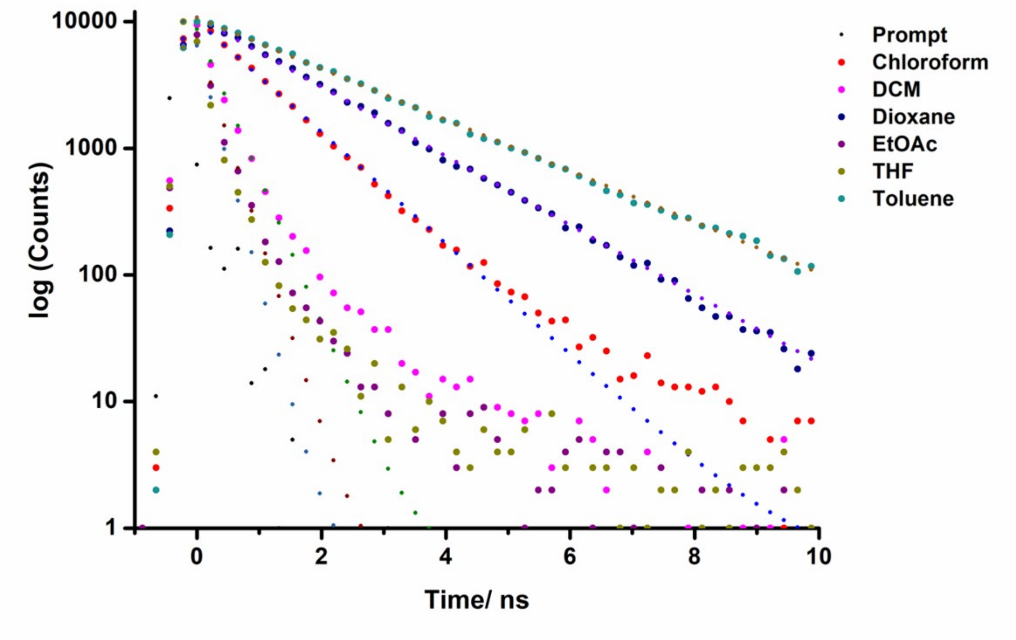


Fig. S4: Solvent-dependent fluorescence decay lifetime of **2a**

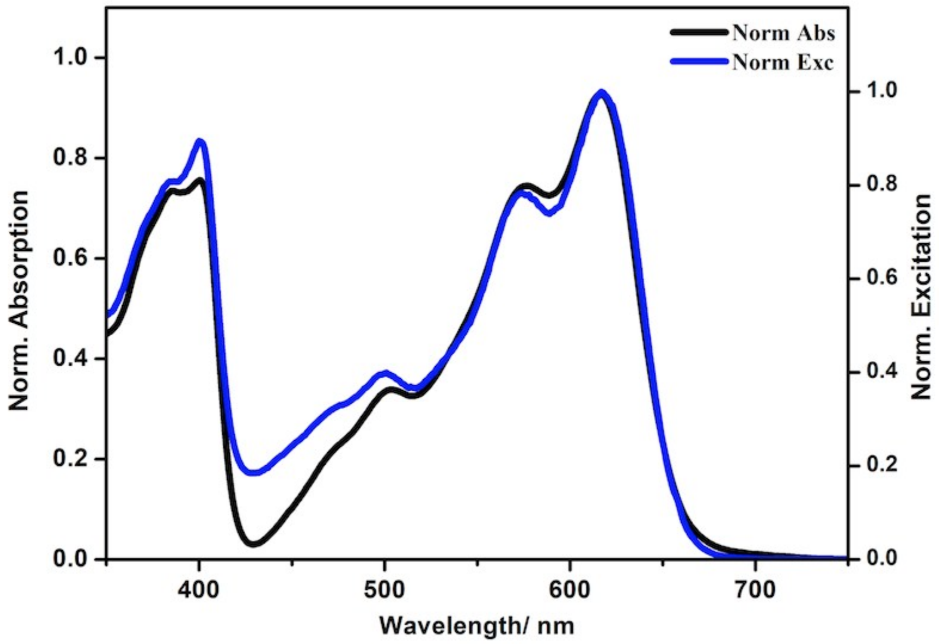


Fig. S5: Verification of optical purity by matching UV-Vis. and excitation spectra of **2b** in Toluene

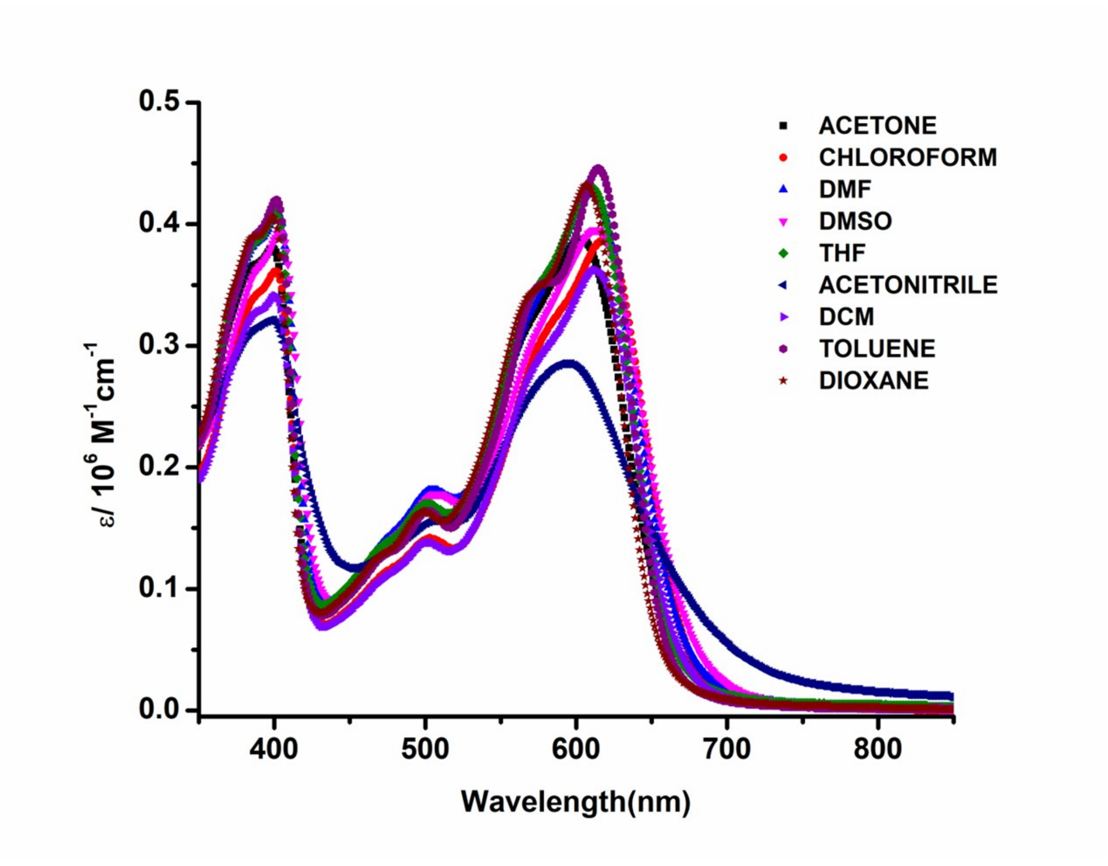


Fig. S6: Solvent-dependent UV-Vis. spectra of **2b** at 5 μM concentration

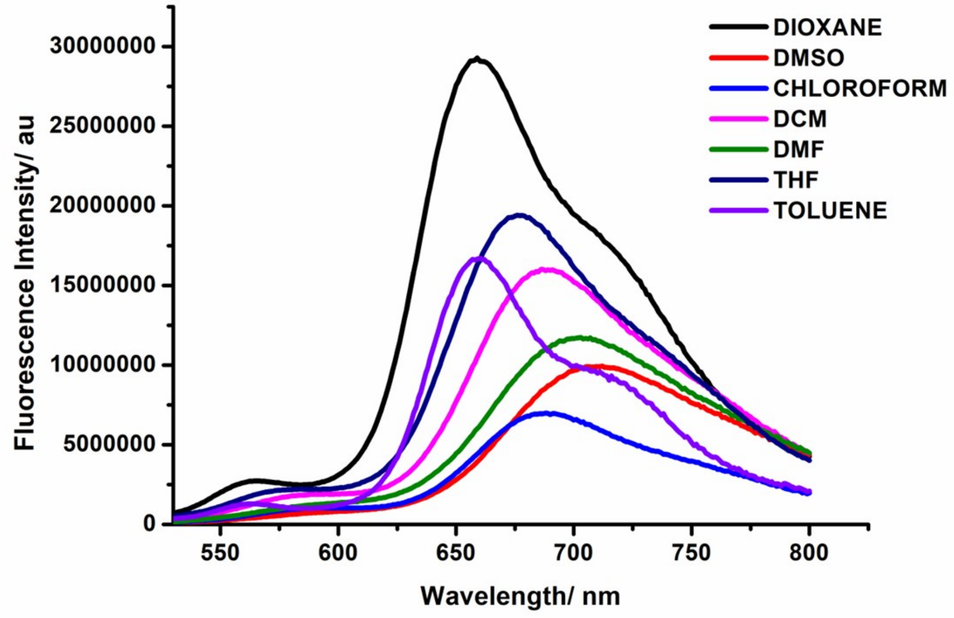


Fig. S7: Solvent-dependent fluorescence spectra of **2b** at 5 μM concentration

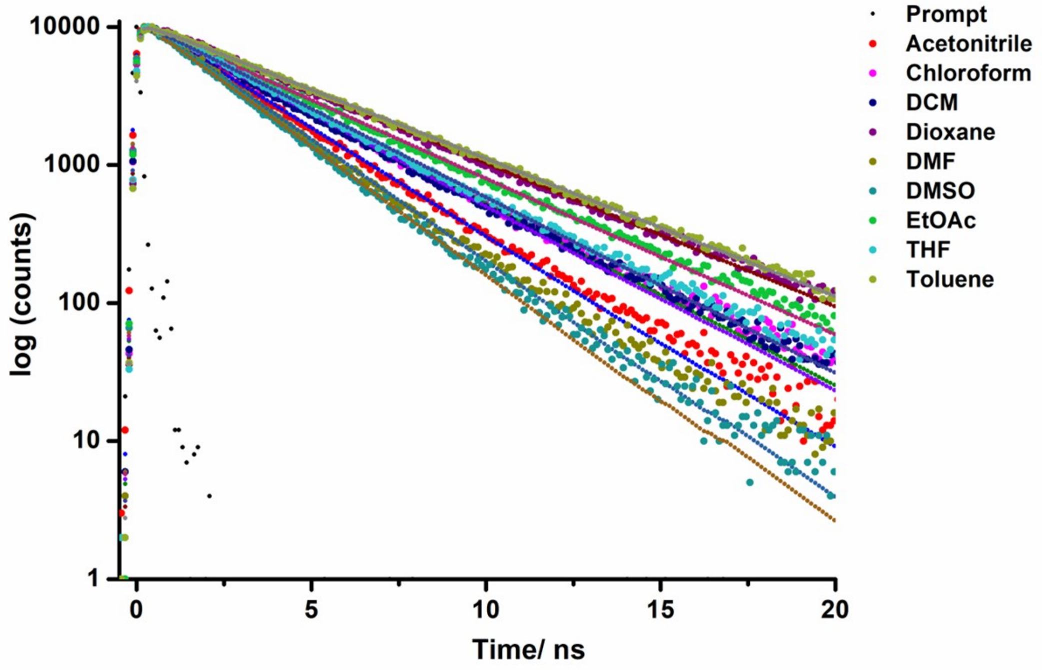


Fig. S8: Solvent-dependent fluorescence lifetime decay of **2b**

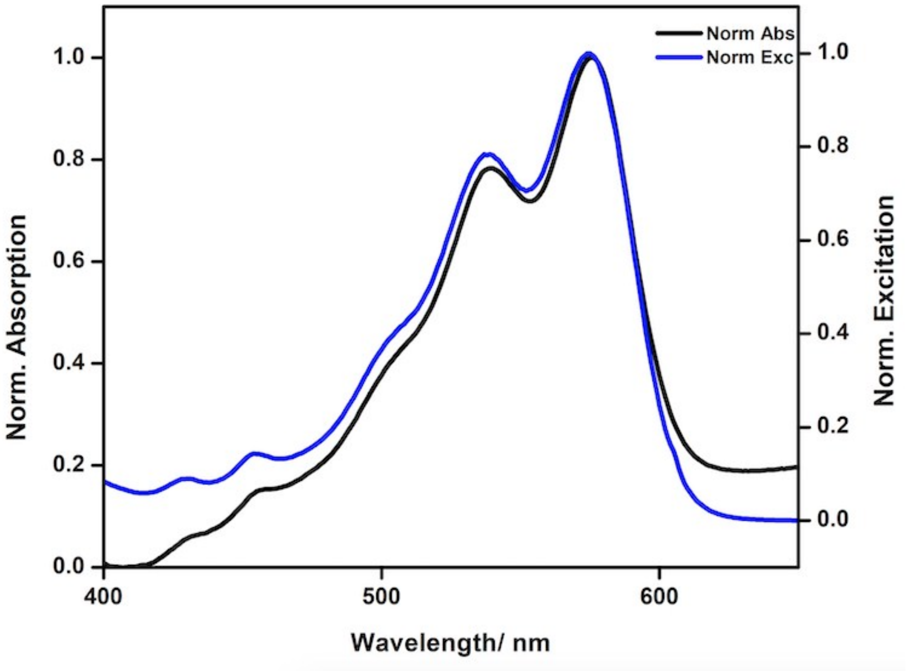


Fig. S9: Verification of optical purity by matching UV-Vis. and excitation spectra of **2c** in Toluene

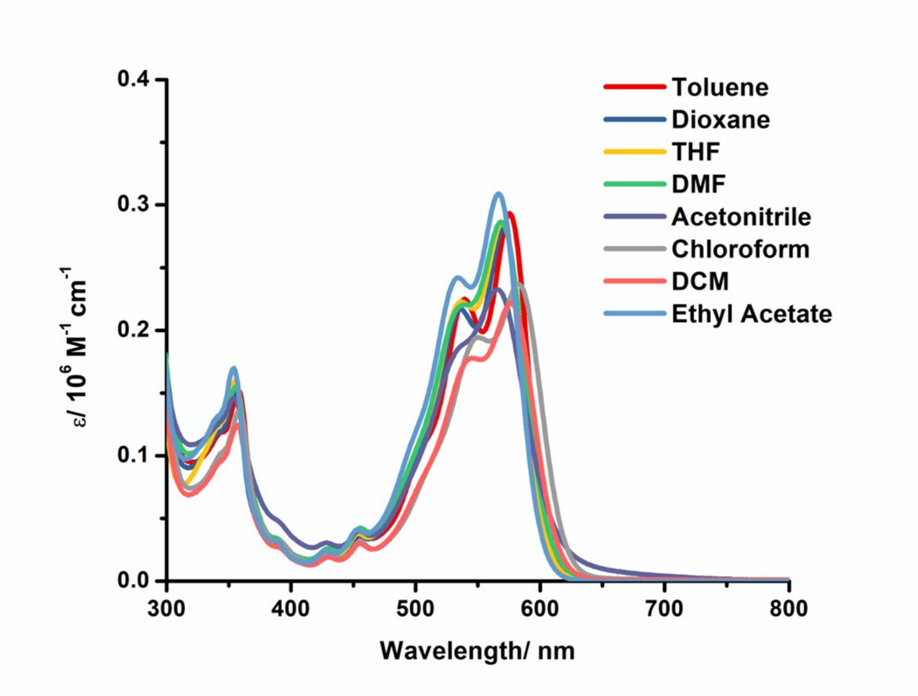


Fig. S10: Solvent-dependent UV-Vis spectra of **2c** at 5 μM concentration

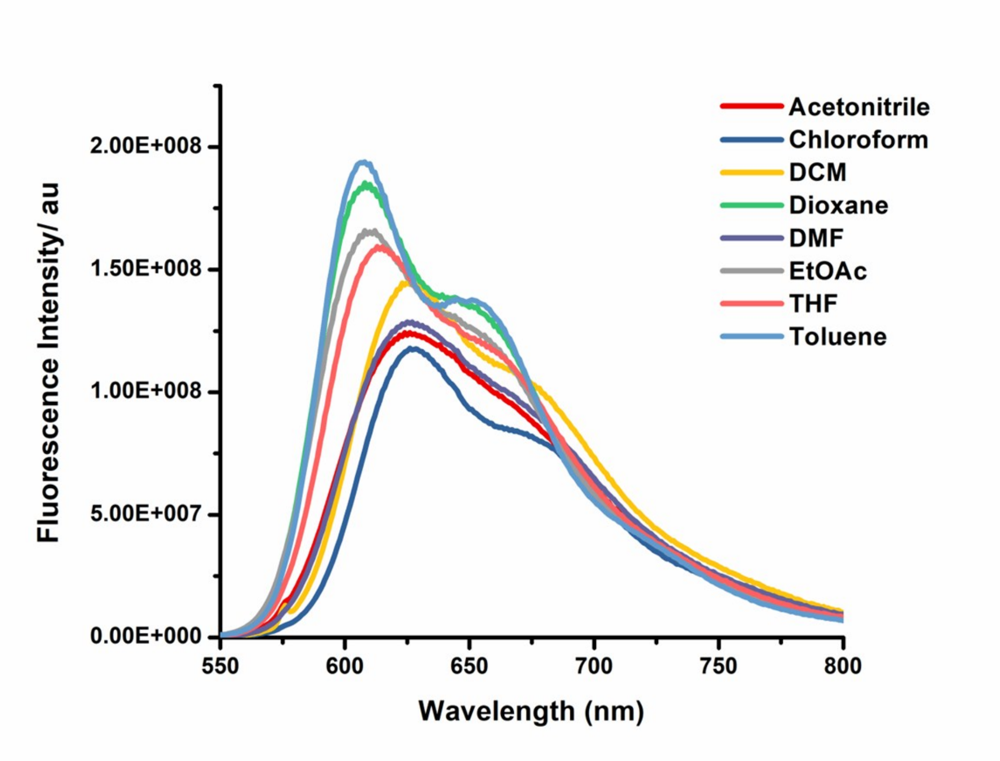


Fig. S11: Solvent-dependent fluorescence spectra of **2c** at 5 μM concentration

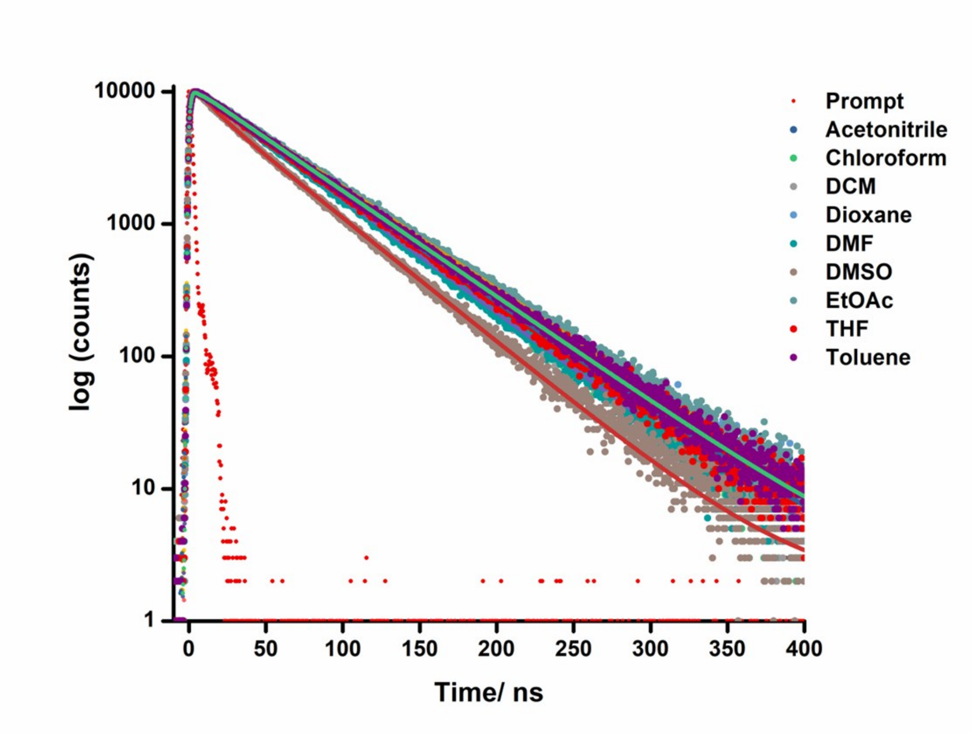


Fig. S12: Solvent-dependent fluorescence decay lifetime of **2c**

Correlation of dipole moment with Stokes shift of PMI derivatives (2a-c):

To understand the solvent effects on the optical properties of fluorophores the fluorophore molecule is considered as a dipole in a continuous solvent dielectric. However, the interactions between solvent molecules and dipoles originated from fluorophores affect the energy difference between the ground and excited states, and results spectral shifts. Lets consider μ_g and μ_e are ground and excited state dipole moments, respectively. The difference of dipole moment can be determined from the Stokes value. In order to get a feel of polarization dependence of spectral profiles, however, the $E_T(30)$ function, i.e. molar transition energy, which is an empirical measure of solvent polarity and is based on solvatochromic behaviour of a betaine dye as a probe solute, is of particular interest. However, to avoid certain dimensionality problems, the normalized $E_T(30)$ function, viz., $E_T(N)$ is often employed.[1] An empirical correlation of spectral shift with $E_T(N)$ has been developed [1] according to which,

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2 - \left(\frac{a_B}{a}\right)^3\right]E_T^N + constant$$

Where $\Delta\mu_B$ and a_B designate dipole moment change on excitation and Onsager radius, respectively, for betaine dye. Similarly, the terms $\Delta\mu$ and 'a' are the corresponding values for the unknown molecule under study. The values of solute radii were in turn estimated by calculating the Van der Waals volumes $(V_{VdW} = {}^4/_3\pi a^3)$ using the reported method.[2]

A linear plot of the Stokes shift versus $E_T(N)$ results in the slope 'm' which can be expressed as: $m = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]$ Where for betaine dye $\Delta\mu_B = 9D$ and a_B 6.2 Å

For compound **2a**: $V_{VdW} = 975.14$ Å^3, a =6.15 Å, slope from figure R2 (a) m=2350 and $\Delta\mu$ (change in dipole moment upon excitation)= 3.49 D

For compound **2b**: $V_{VdW} = 897.02$ Å^3, a=5.98 Å, slope from figure R2(b), m=3463 and $\Delta\mu$ $(change\ in\ dipole\ moment\ upon\ excitation)$= 4.75 D

For compound **2c**: $V_{VdW} = 1267.02$ Å^3, a=6.71 Å, slope from figure R2(c), m=2306 and $\Delta\mu(change\ in\ dipole\ moment\ upon\ excitation)$= 4. 75 D

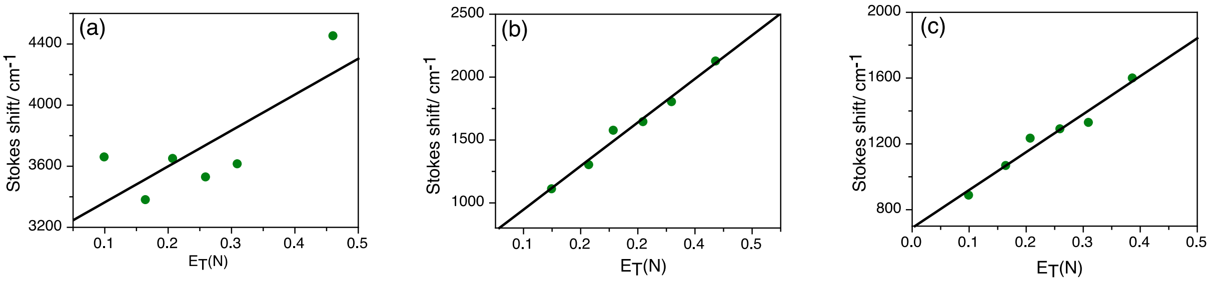


Fig. S13: Plot of Stokes shift versus solvent polarity parameter E_T(N) for (a) **2a**, (b) **2b**, and (c) **2c**.

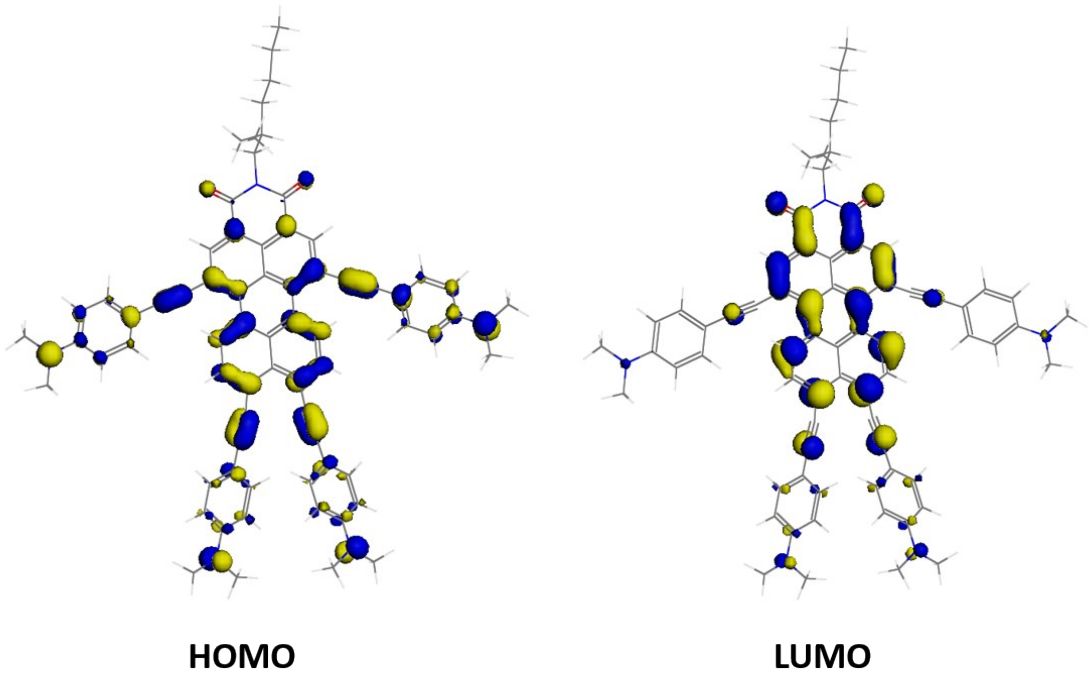
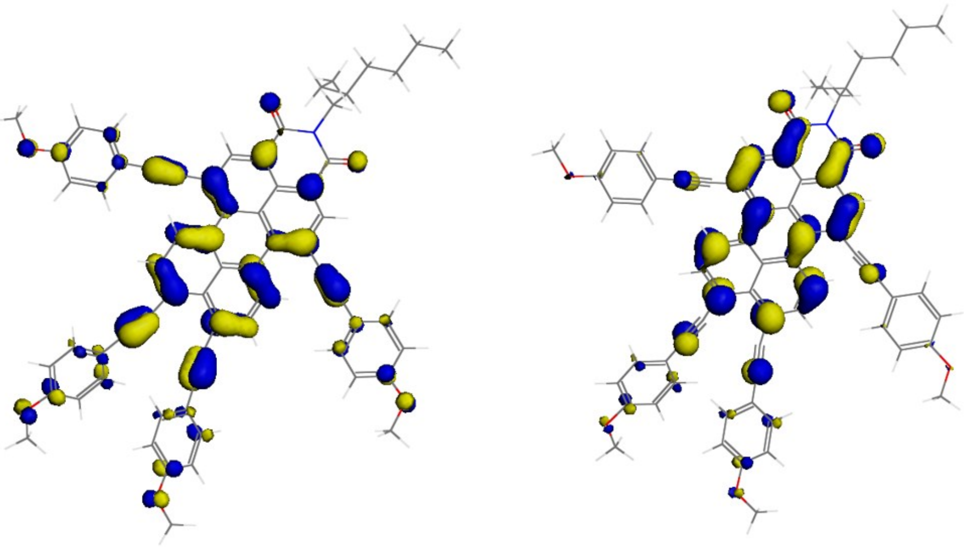


Fig. S14: Frontier molecular orbital profiles of molecules **2a**



HOMO LUMO

Fig. S15: Frontier molecular orbital profiles of molecules **2b**

Solar-cell device fabrication: The device fabrication process and the device structure have been given in supplementary information. In brief, the solar cell has been composed in traditional configuration, *i.e.*, the transparent electrode, indium tin oxide (ITO) was the anode. A bare device without any buffer layer has been prepared. The band diagram of the device is also given as Figure S16.

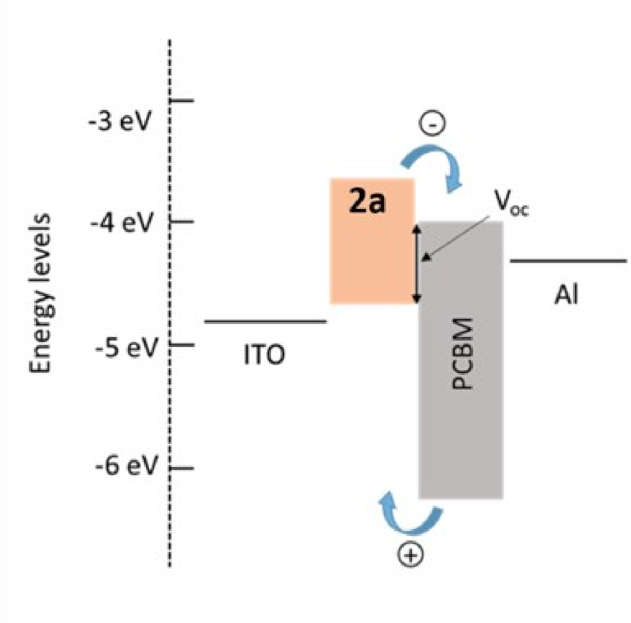


Fig. S16: Band-diagram of the bare solar cell prepared from **2a** and PCBM.

X-ray crystallography:

Suitable crystals for X-ray crystallography were obtained grown by slow diffusion of methanol into a solution of the compound **2c** in hexane. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo K_α (λ = 0.71073 Å) radiation at room temperature.

Empirical formula: $C_{74}H_{107}NO_2Si_4$

Formula weight: 1155.02 g/mol

Temperature / Wavelength: 296(2) K_α 0.71073 Å

Crystal system / space group: Triclinic P–1

Unit cell dimensions: a = 12.0158(4) Å, b = 15.2970(4) Å, c = 21.9620(7) Å, α = 71.487(2) °, β = 74.306(2) °, γ = 67.734(2) °

Unit cell volume / units Z: 3490.2(2) Å^3 4

Absorption coefficient / F(000): 0.257 mm^{-1}

Θ-range for data collection: 0.992 to 28.283 °

Limiting indices: -16≤h≤15 20≤k≤20 -29≤l≤27

Reflections collected / unique: 9907/ 8036 [R_{int} = 0.1360]

Reflections observed [I > 2□(I)]: 8036

Completeness to Θ = 25.242, 89.2%

Absorption correction: Semi-emperical from equivalents

Goodness-of-fit on F^2: 1.415

Final R indices [I > 2σ (I)]: R1 = 0.1360 ωR2 = 0.4512

R indices (all data): R1 = 0.2330 ωR2 = 0.3923

Largest diff. peak and hole: 1.508 and -1.163 e/Å^3

CCDC number: 1911385

Characterization: ^{1}H-NMR, ^{13}C{^{1}H}-NMR and mass spectra of the synthesized compounds

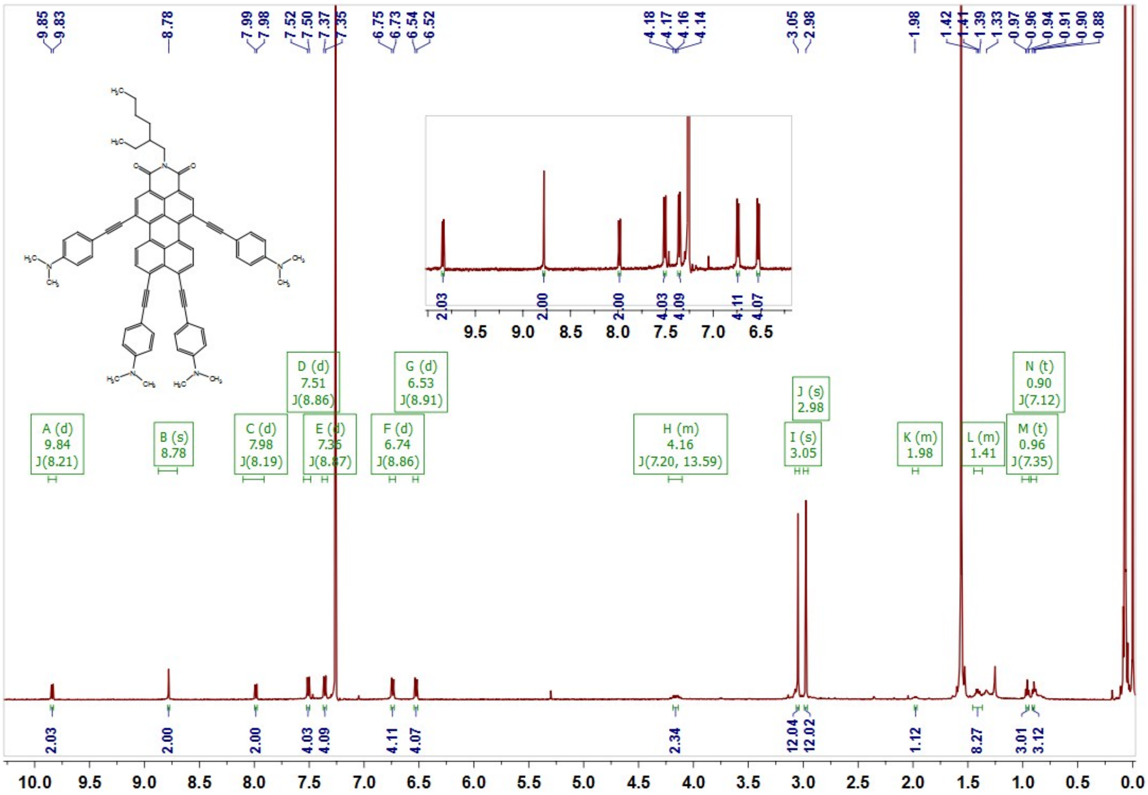


Fig. S17: ^{1}H NMR spectrum of compound **2a** recorded in $CDCl_3$ at 500 MHz

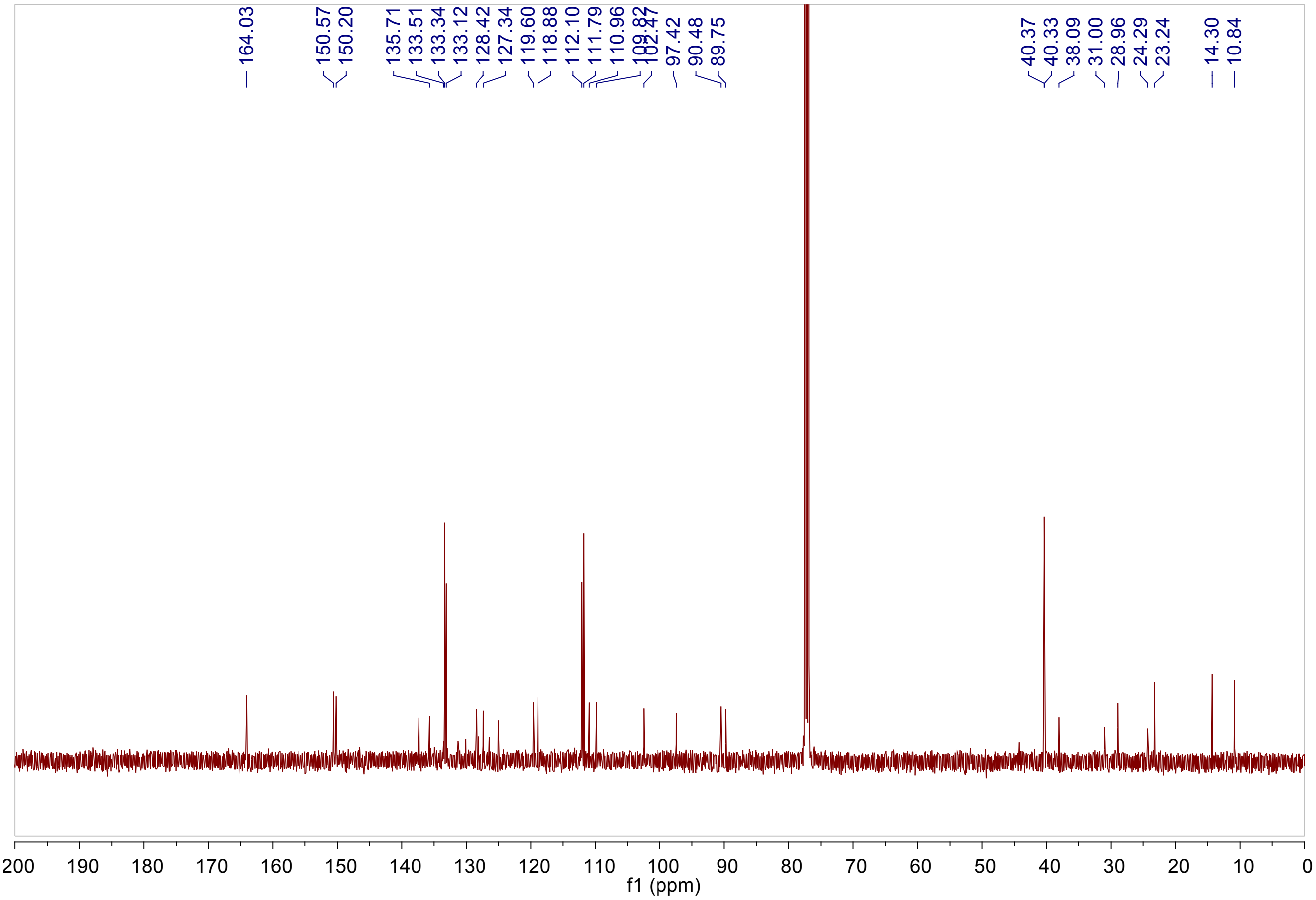


Fig. S18: ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$ at 126 MHz

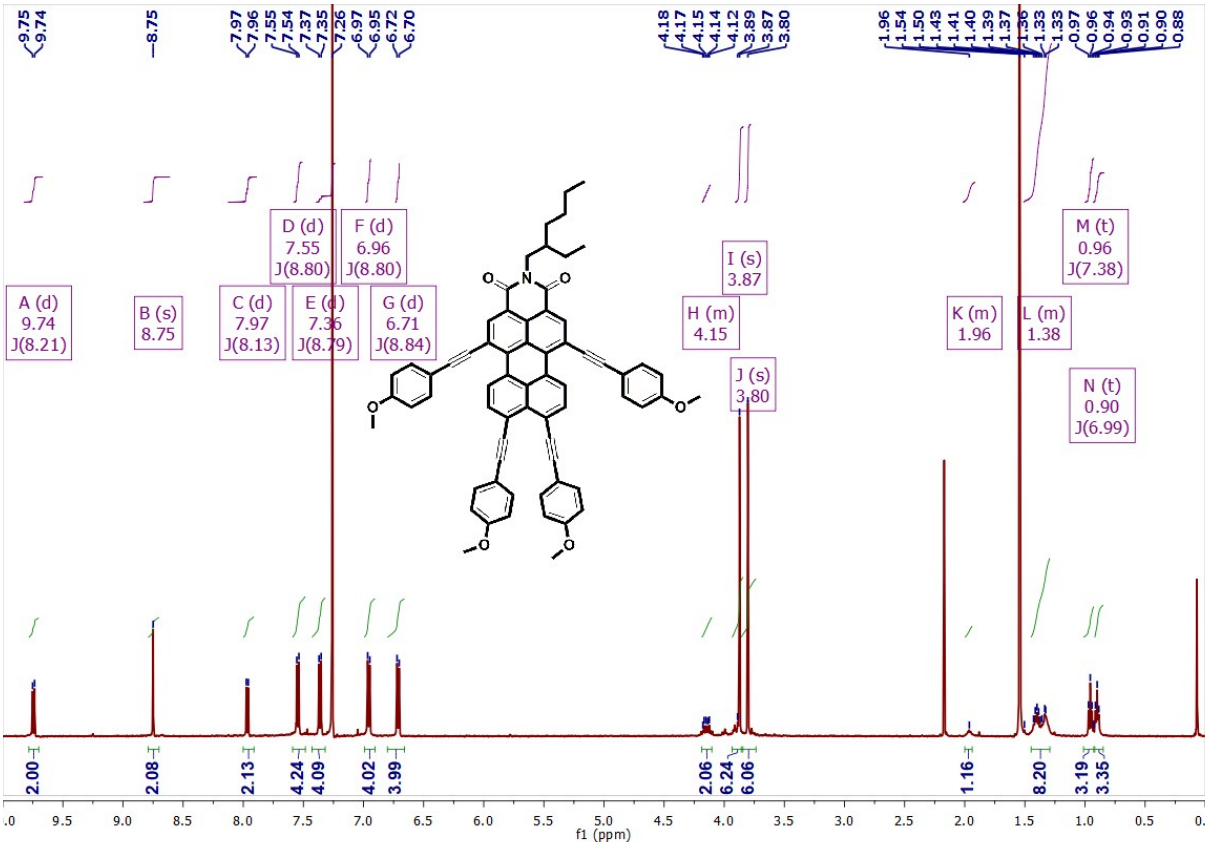


Fig. S19: ^{1}H NMR spectrum of compound **2b** recorded in $CDCl_3$ at 500 MHz

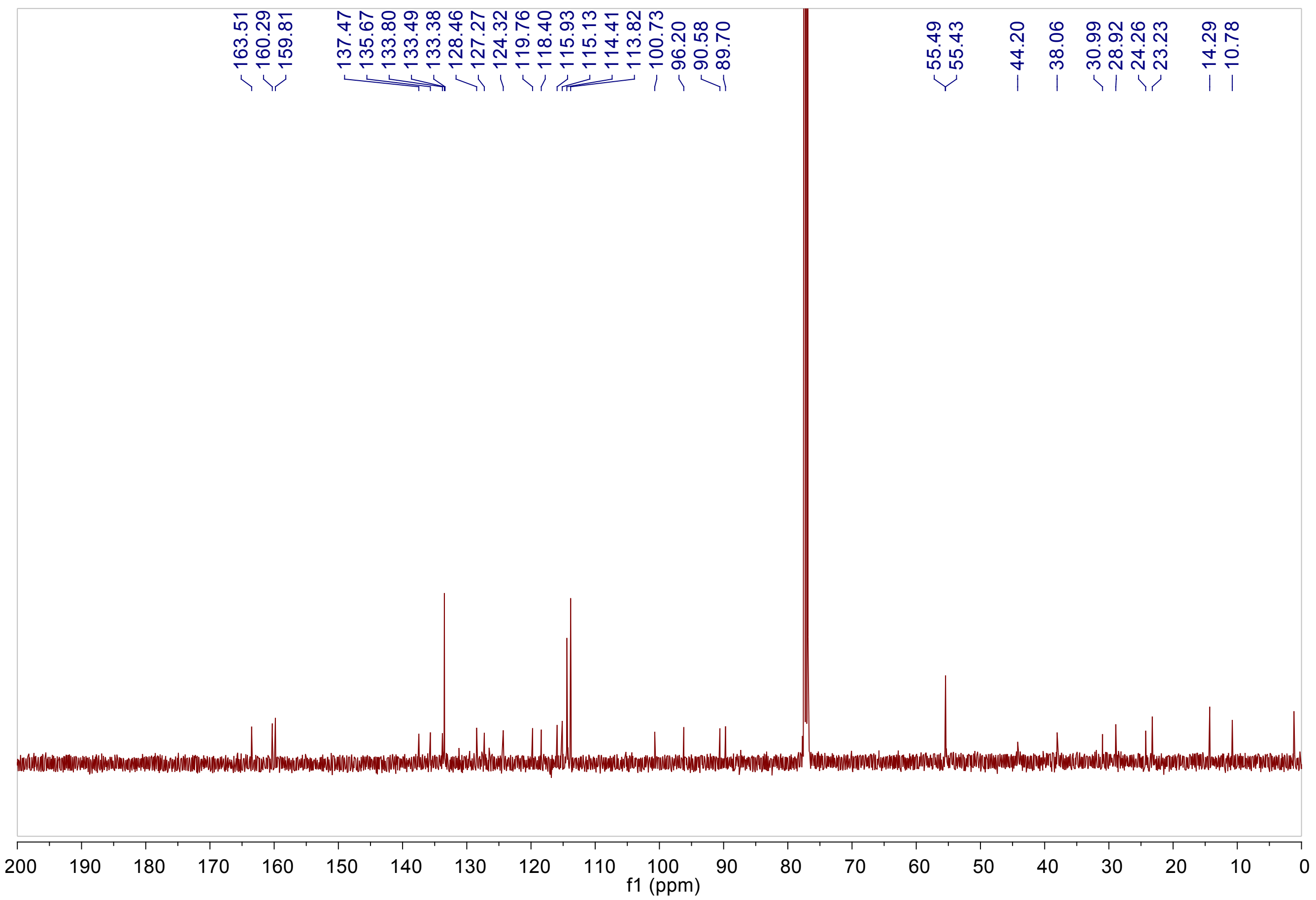


Fig. S20: ^{13}C NMR spectrum of compound **2b** recorded in $CDCl_3$ at 126 MHz

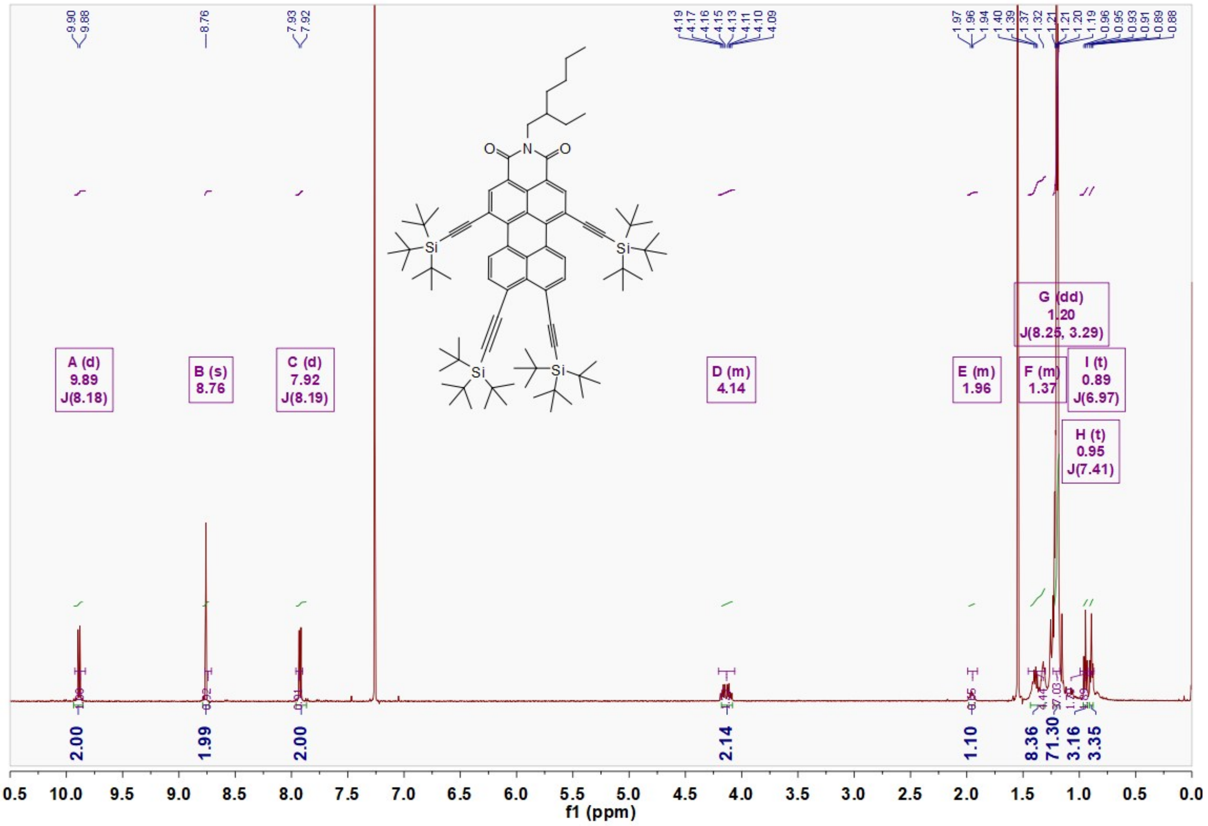


Fig. S21: ^{1}H NMR spectrum of compound **2c** recorded in $CDCl_3$ at 500 MHz

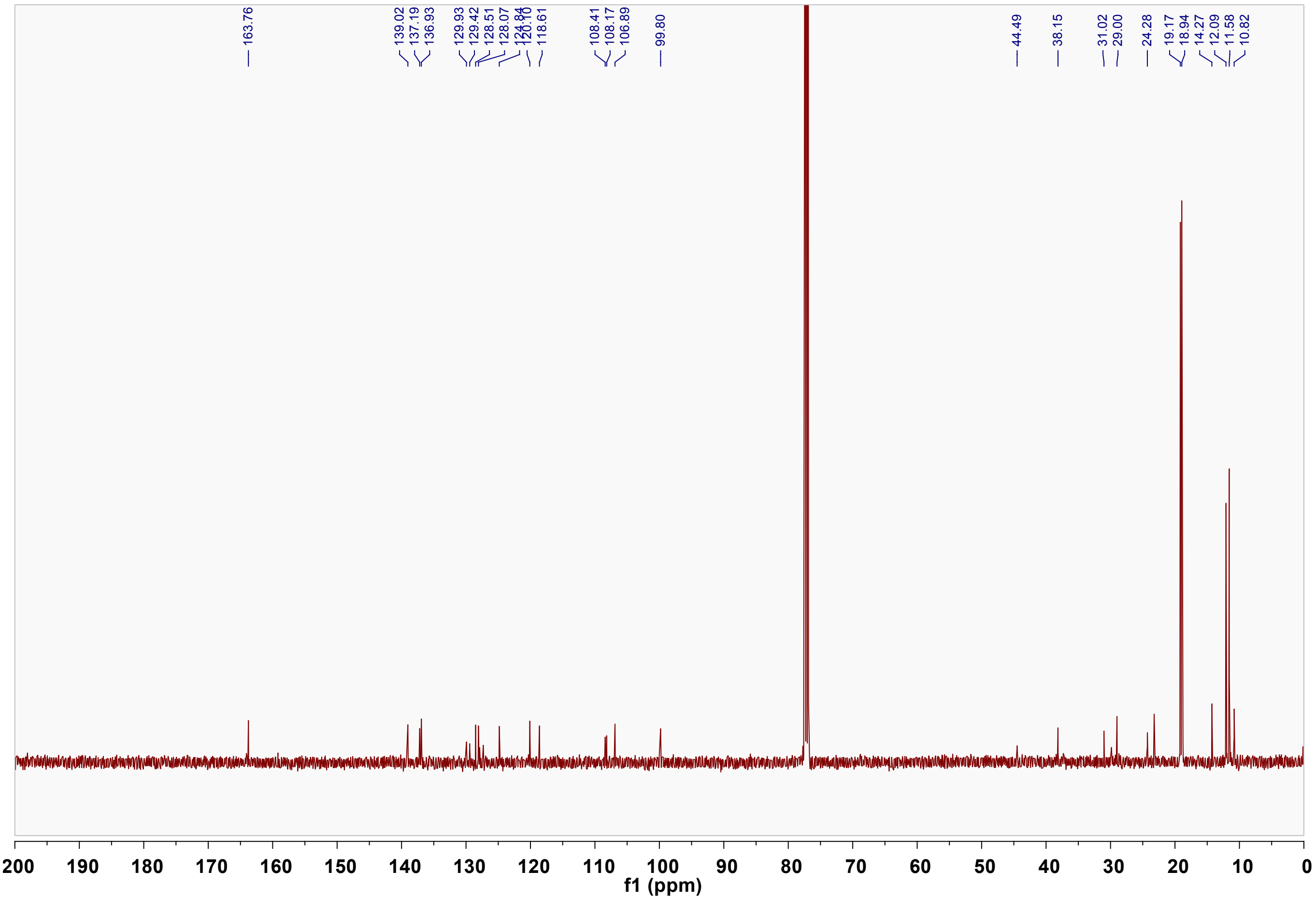


Fig. S22: ^{13}C NMR spectrum of compound **2c** recorded in $CDCl_3$ at 126 MHz

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste

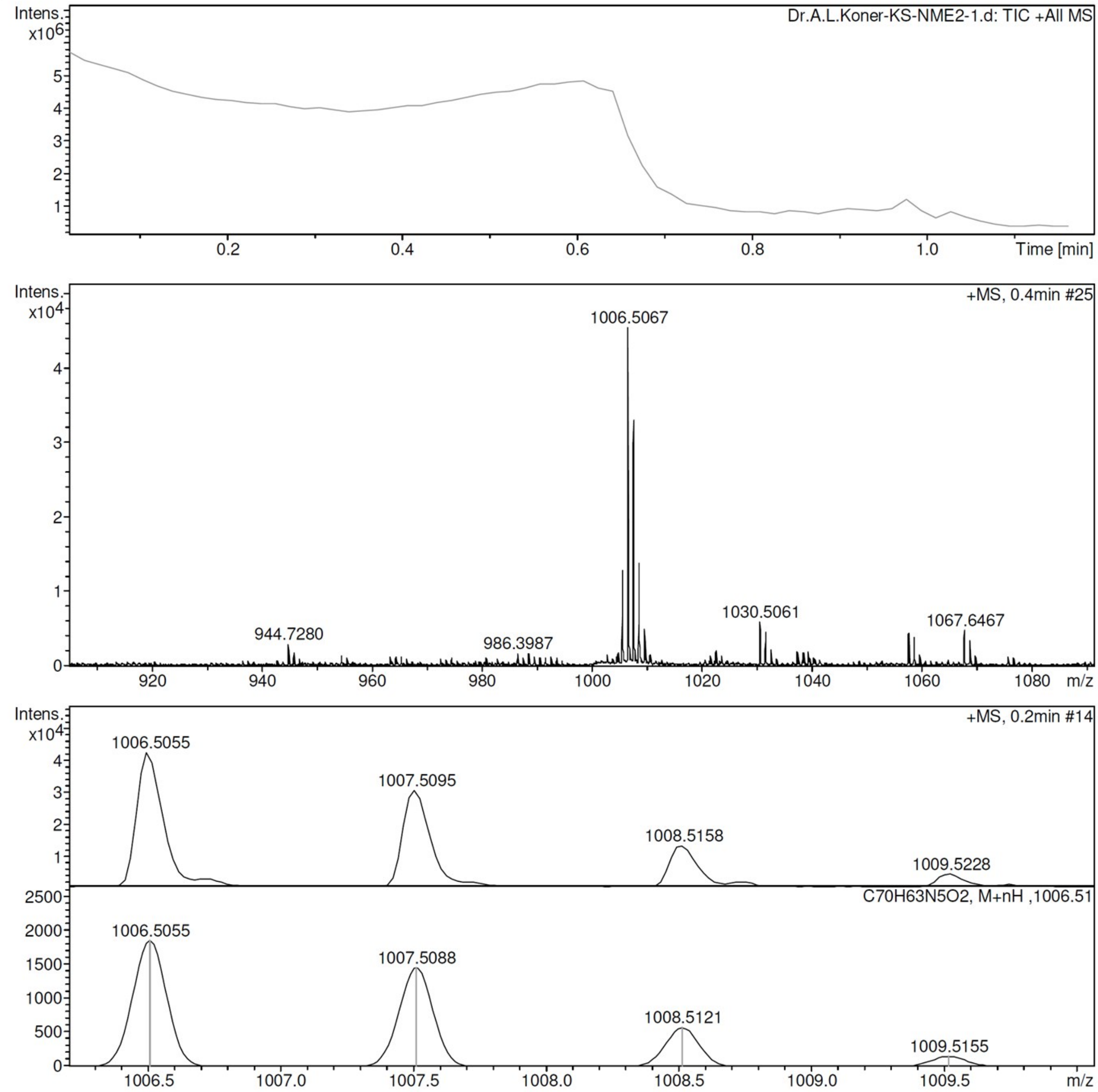


Fig. S23: Mass spectrum of compound **2a**

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste

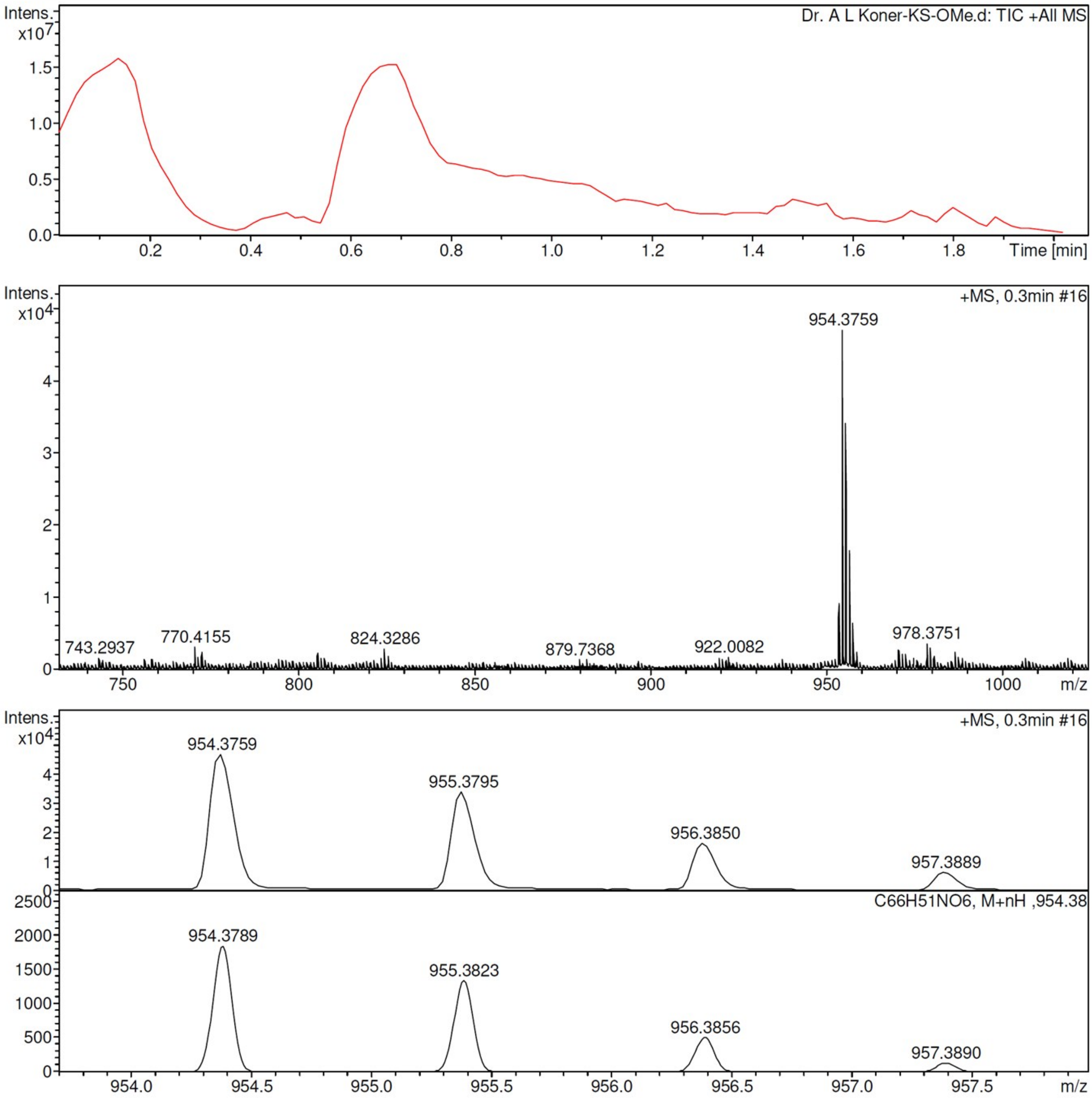


Fig. S24: Mass spectrum of compound **2b**

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste

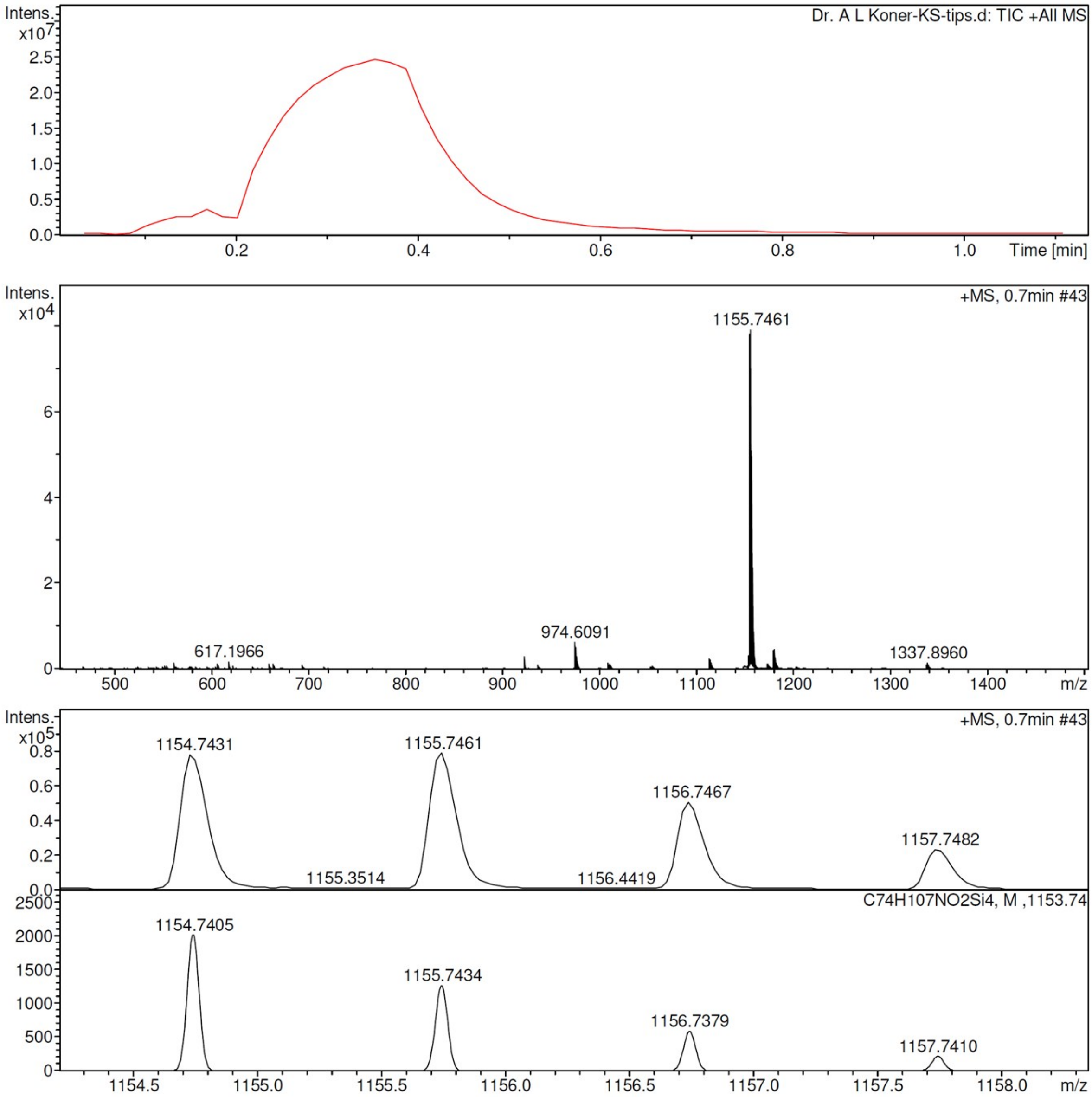


Fig. S25: Mass spectrum of compound **2c**

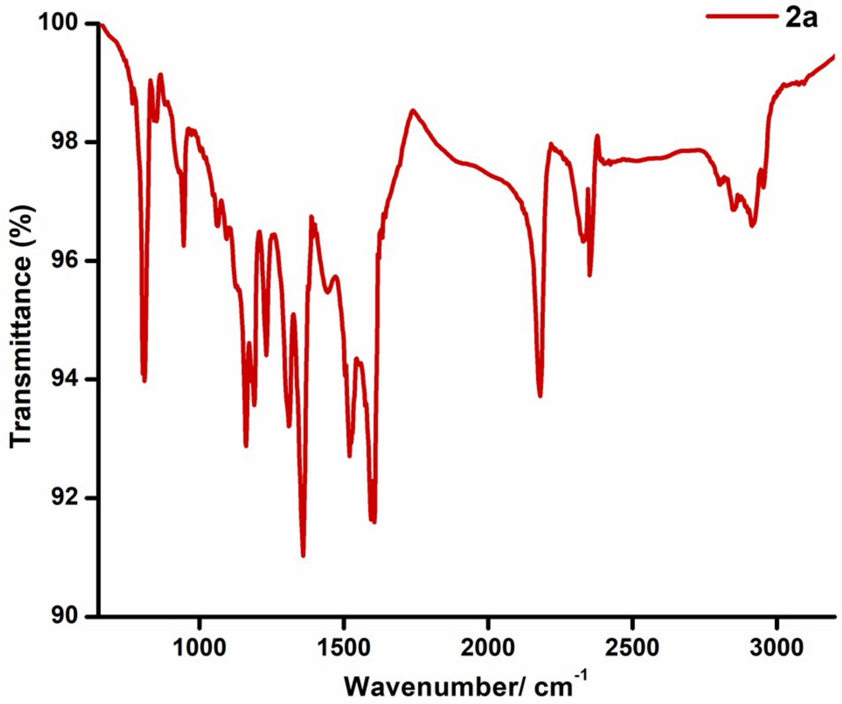


Fig. S26: IR spectrum of compound **2a**

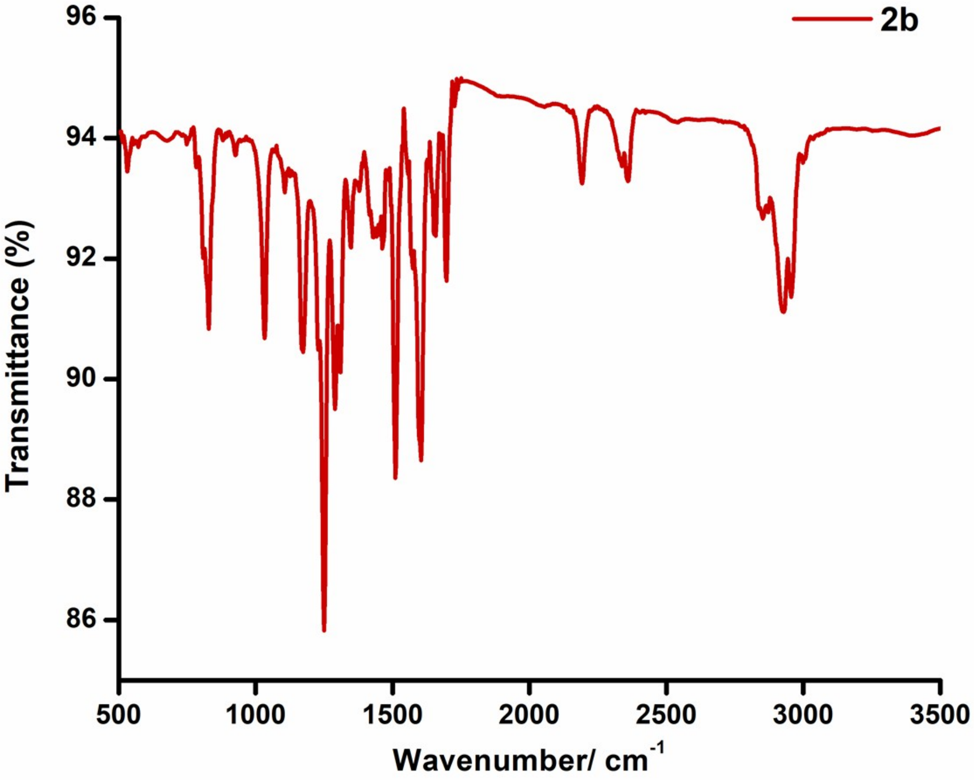


Fig. S27: IR spectrum of compound **2b**

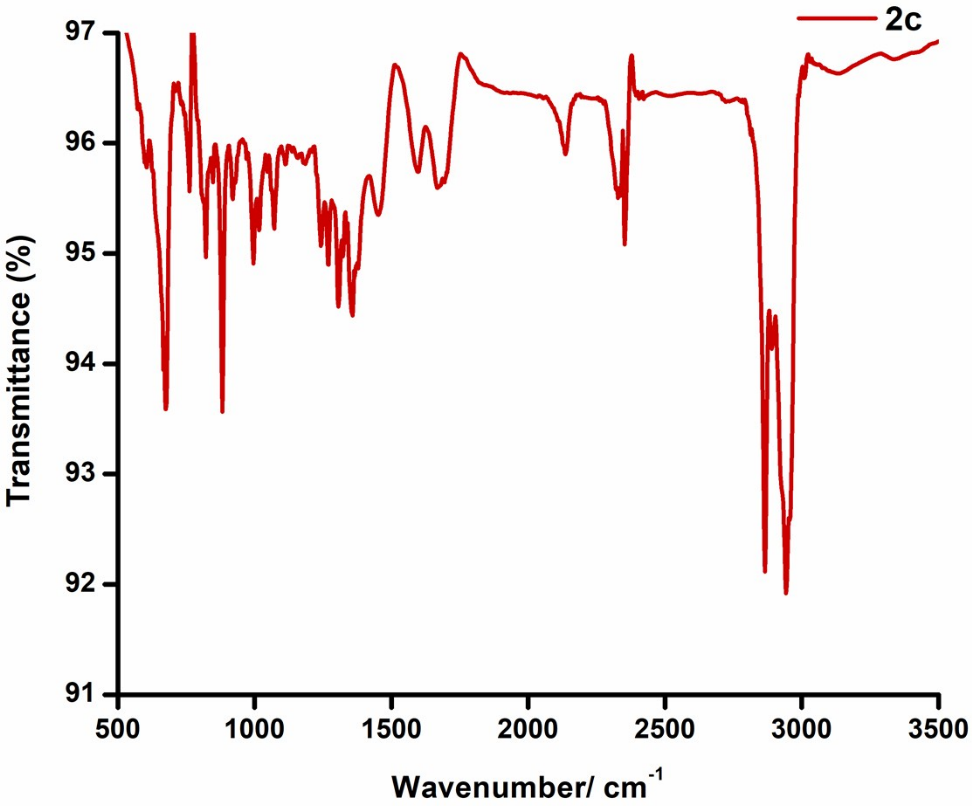


Fig. S28: IR spectrum of compound **2c**

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