

Supplementary Information for

**C-C coupling over Schiff base condensation: a rational design
strategy for a strongly fluorescent molecular material**

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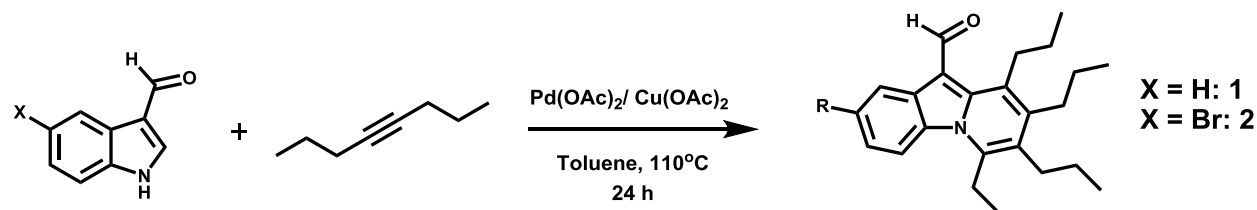
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I. Synthesis and Characterization

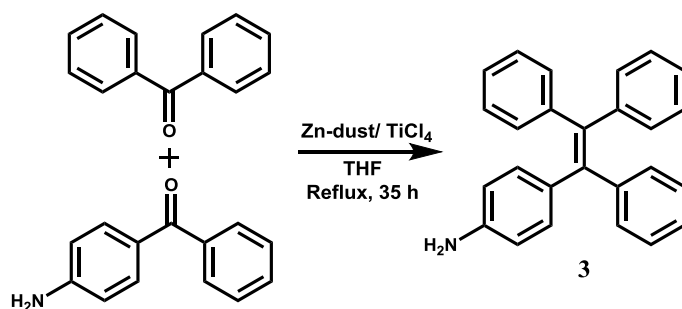
Instrumentation: ^1H and ^{13}C -NMR spectra were recorded on Bruker Avance III 500 MHz NMR spectrometer and the chemical shifts (δ) are reported in parts per million (ppm) using residual solvent signals as internal standards. FTIR measurements were carried out on Perkin Elmer FTIR spectrophotometer. Ten scans were signal-averaged, with a resolution of 2 cm^{-1} at room temperature. KBr pellet was used for the measurements. The surface morphology and size of the nanoparticles were examined using Carl Zeiss (Ultraplus) field emission scanning electron microscope (FESEM).

Chemicals: All chemicals were used as received unless stated otherwise. Indole-3-carboxaldehyde (97%), 5-bromo-3-carboxaldehyde (98%), 4-octyne (99%), copper(II) acetate monohydrate (99%), palladium(II) acetate (99.9%), 4-aminobenzophenone (90%), 4-bromobenzophenone (98%), diphenylmethane (99%), p-toluenesulfonic acid monohydrate (98.5%), bis(pinacolato)diboron (99%), [1,1'-bis(diphenylphosphino)ferrocene]-dichloropalladium(II) complex with dichloromethane, bis(triphenylphosphine)palladium(II) dichloride (98%), dimethyl sulfoxide (99%), toluene (99.85%), tetrakis(triphenylphosphine)palladium(0) (99.9%), L-cysteine(97%), DL-homocysteine (95%) and triethylamine (99%) were received from Sigma-Aldrich. Sodium hydroxide (99%), potassium carbonate, acetic acid, 1,2-dioxane, chloroform and hexane were received from Merck. THF (99%), trifluoroacetic acid, ethanol (99.8%), extra pure concentrated HCl were received from Spectrochem.

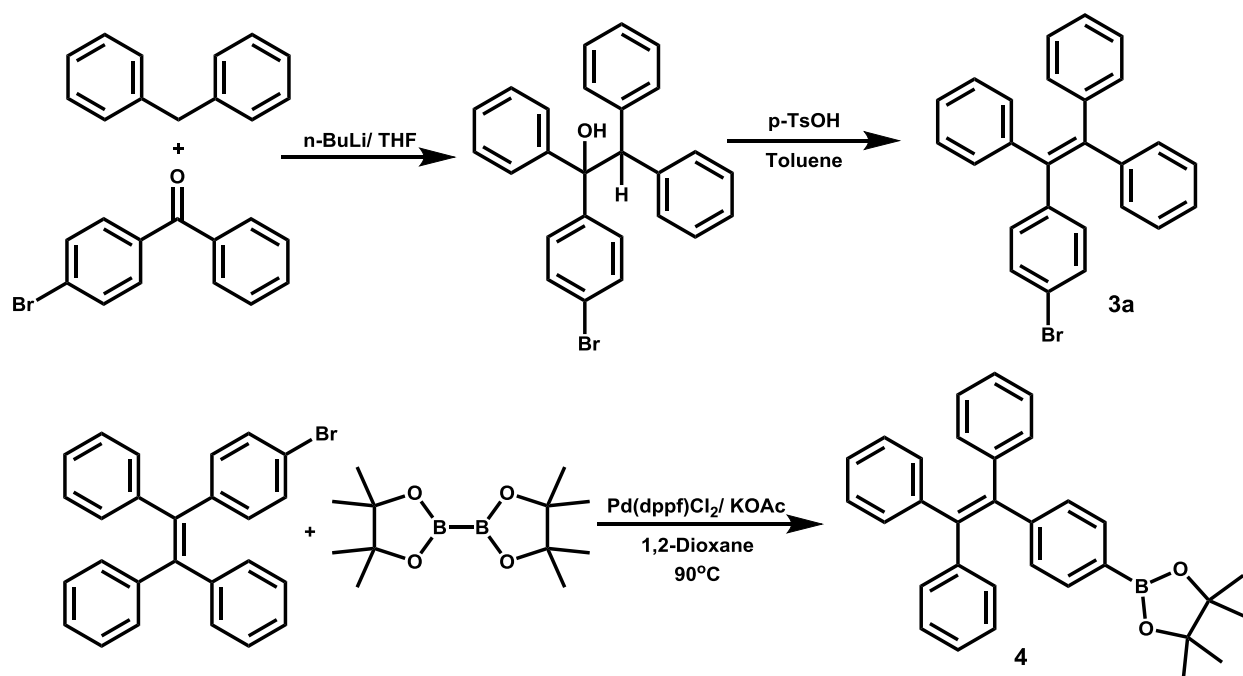
Reaction schemes:



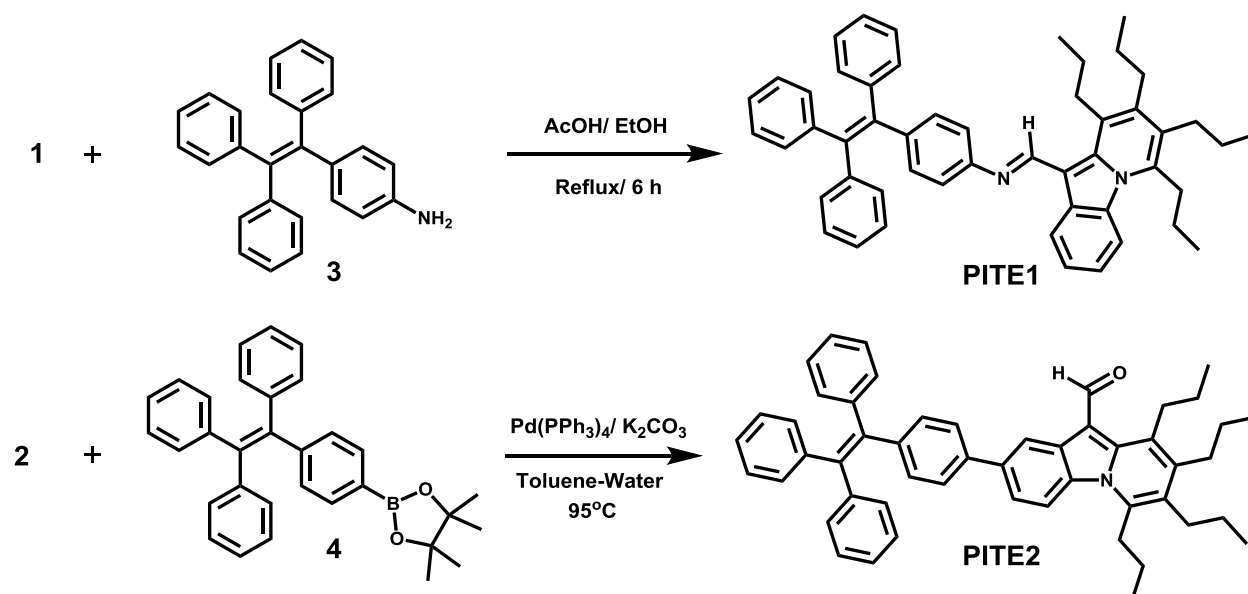
Scheme S1. Synthesis of pyrido[1,2-a]indole derivatives (**1**, **2**).¹



Scheme S2. Synthesis of 1-(4-aminophenyl)-1,2,2-triphenylethene (**3**).²



Scheme S3. Synthesis of 1-(4-bromophenyl)-1,2,2-triphenylethylene (**3a**) and 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl) phenyl)-1,3,2-dioxaborolane (**4**).³



Scheme S4. Synthesis of **PITE1** and **PITE2**.

Synthesis of compounds **1** and **2**:

In a 100 mL round-bottom flask, substituted 3-carboxaldehyde (1 eqv.) and 4-octyne (2 eqv.) were stirred in toluene (10 mL) at RT and purged with argon for 5 min. Pd(OAc)₂ (5 mol %) and Cu(OAc)₂ (1.8 eqv.) were added to the resultant clear solution, which was further purged with argon for 5 min. The reaction mixture was stirred at 110°C for 36 h. After completion the reaction was quenched with water and the mixture was extracted with ethyl acetate. The resulting organic solution was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated. The resulting residue was purified by silica gel flash column chromatography (EtOAc/hexane) to afford **1** and **2**. The ¹H NMR data for the compounds are given below.

1: ¹H NMR: δ_H (500 MHz, CDCl₃) 10.46 (1 H, s), 9.01 (1 H, d, *J* 8.1), 7.94 (1 H, d, *J* 8.7), 7.49 (1 H, q, *J* 7.0), 7.34 – 7.28 (1 H, m), 3.38 – 3.26 (2 H, m), 3.09 – 2.98 (2 H, m), 2.77 – 2.61 (4 H, m), 1.99 – 1.83 (2 H, m), 1.78 (2 H, tt, *J* 15.1, 7.4), 1.68 – 1.51 (4 H, m), 1.29 – 1.19 (3 H, m), 1.11 (9 H, dd, *J* 13.7, 7.2).

¹³C NMR: δ_C (126 MHz, CDCl₃) 184.25, 143.44, 142.61, 139.71, 131.86, 130.36, 128.41, 125.65, 124.61, 122.84, 121.91, 115.41, 107.42, 32.79, 31.81, 31.72, 30.83, 24.77, 24.23, 22.20, 21.35, 14.90, 14.74, 14.30, 13.85.

FTIR (frequency/cm⁻¹): 2960, 2870, 1616, 1470, 1380, 732.

MS (MALDI-ToF): Calculated for C₂₅H₃₃NO is 363.26 and found 363.140.

2: ¹H NMR: δ_H (500 MHz, CDCl₃) 10.43 (1 H, s), 9.21 (1 H, d, *J* 2.2), 7.79 (1 H, d, *J* 9.2), 7.41 (1 H, dd, *J* 9.2, 2.2), 3.36 – 3.26 (2 H, m), 3.07 – 2.99 (2 H, m), 2.78 – 2.64 (4 H, m), 1.95 – 1.83 (2 H, m), 1.78 (2 H, dt, *J* 19.4, 7.5), 1.66 – 1.53 (4 H, m), 1.29 – 1.19 (3 H, m), 1.19 – 1.10 (9 H, m).

¹³C NMR: δ_C (126 MHz, CDCl₃) 184.18, 143.64, 143.22, 139.56, 131.89, 130.48, 128.47, 125.15, 125.05, 124.70, 119.80, 116.68, 106.81, 32.73, 31.76, 31.74, 30.83, 24.73, 24.21, 22.18, 21.13, 14.90, 14.73, 14.28, 13.81.

FTIR (frequency/cm⁻¹): 2956, 2930, 2872, 1624, 1440, 778.

MS (MALDI-ToF): Calculated for C₂₅H₃₂BrNO is 441.17 and found 442.13 (M+1).

Synthesis of 1-(4-aminophenyl)-1,2,2-triphenylethene (3):

In a two-necked RB flask equipped with a magnetic stirrer, zinc powder (2.6 g, 40.7 mmol) and 40 mL of THF were added. After the mixture was cooled to –5°C, TiCl₄ (2.2 mL, 20.3 mmol) was slowly added by a syringe. The mixture was brought to room temperature and stirred for 30 min and then refluxed for 3 h. A solution of benzophenone (1.1 g, 6.1 mmol) and 4-aminobenzophenone (1 g, 5.1 mmol) in 20 mL THF was added slowly. After complete addition, the reaction mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was quenched with 10% aqueous solution of K₂CO₃ and then extracted with dichloromethane. The organic layer was collected and concentrated. The crude product was purified by silica-gel column chromatography to give a light yellow solid in 48% yield (845 mg).

¹H NMR: δ_H (500 MHz, CDCl₃) 7.17 – 6.95 (15 H, m), 6.85 – 6.74 (2 H, m), 6.46 – 6.37 (2 H, m), 3.58 (2 H, s).

¹³C NMR: δ_C (126 MHz, CDCl₃) 144.78, 144.35, 144.22, 144.18, 140.95, 139.32, 134.03, 132.49, 131.47, 131.41, 131.36, 127.67, 127.54, 127.51, 126.24, 126.06, 114.32.

FTIR (frequency/cm⁻¹): 3440-3480 (broad), 3380, 3022, 1618, 1512, 1280.

MS (MALDI-ToF): Calculated for C₂₆H₂₁N is 347.17 and found 347.05.

Synthesis of 1-(4-bromophenyl)-1,2,2-triphenylethylene (**3a**):

To a solution of diphenylmethane (1 g, 6.0 mmol) in dry tetrahydrofuran (10 mL), 2 mL of 2.5 M solution of *n*-butyllithium in hexane (10 mmol) was added at 0°C under an argon atmosphere. The resulting orange-red solution was stirred for 45 min at 0°C. To this solution an appropriate amount of 4-bromobenzophenone (1.2 g, 4.5 mmol) was added, and the reaction mixture was brought to room temperature and stirred for 6 h. Then the reaction mixture was quenched with the addition of an aqueous solution of ammonium chloride (10%), the organic layer was extracted with dichloromethane (3 × 50 mL), and the combined organic layers were washed with a saturated brine solution and dried over anhydrous MgSO₄. The solvent was evaporated, and the resulting crude alcohol (containing excess diphenylmethane) was subjected to acid-catalyzed dehydration as follows.

The crude alcohol was dissolved in a 30 mL of toluene in a 100 mL RB flask fitted with a Dean-Stark trap. A catalytic amount of *p*-toluenesulphonic acid (0.2 g, 1.2 mmol) was added, and the mixture was refluxed for 3-4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous NaHCO₃ solution (2 × 25 mL) and dried over anhydrous MgSO₄ and evaporated to afford **3a**. The crude product was purified by a simple silica gel column chromatography from a mixture of dichloromethane and hexane to give the target compound as white solid in yield 50% (1.23 g).

¹H NMR: δ_H (500 MHz, CDCl₃) 7.22 (2 H, d, *J* 8.5), 7.14 – 7.08 (9 H, m), 7.04 – 6.99 (6 H, m), 6.90 (2 H, d, *J* 8.5).

¹³C NMR: δ_C (126 MHz, CDCl₃) 143.41, 143.33, 143.22, 142.70, 141.61, 139.66, 132.98, 131.30, 131.25, 131.23, 130.85, 127.88, 127.78, 127.68, 126.70, 126.65, 126.60, 120.45.

FTIR (frequency/cm⁻¹): 3074, 3022, 1598, 1490, 1070, 692.

MS (MALDI-ToF): Calculated for C₂₆H₁₉Br is 410.07 and found 410.962.

Synthesis of 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl) phenyl)-1,3,2-dioxaborolane (**4**):

A mixture of **3a** (0.4 g, 0.97 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (0.35 g, 1.4 mmol), [Pd(dppf)]Cl₂ (0.024 g, 0.03 mmol), and potassium acetate (0.3 g, 3.5 mmol) in degassed 1,2-dioxane (10 mL) was stirred at 90°C for 24 h. The reaction was quenched by

adding water, and the mixture was washed with dichloromethane. The organic layer was collected, dried over MgSO_4 and concentrated in vacuum. The crude product was then purified by silica gel column chromatography (hexane/dichloromethane) to give the target compound as white solid in 67% yield (300 mg).

$^1\text{H NMR}$: δ_{H} (500 MHz, CDCl_3) 7.54 (2 H, d, J 8.2), 7.12 – 7.06 (9 H, m), 7.06 – 6.98 (8 H, m), 1.32 (12 H, s).

$^{13}\text{C NMR}$: δ_{C} (126 MHz, CDCl_3) 146.76, 143.69, 143.59, 143.51, 141.37, 140.84, 134.08, 131.35, 131.32, 131.30, 130.69, 127.72, 127.63, 126.52, 126.45, 126.43, 83.69, 24.91.

FTIR (frequency/ cm^{-1}): 2982, 1608, 1360, 1147, 700.

MS (MALDI-ToF): calculated for $\text{C}_{32}\text{H}_{31}\text{BO}_2$ is 458.41 and found 458.292.

Synthesis of 1-(1,2,3,4-tetrapropyl-4aH-fluoren-9-yl)-N-(4-(1,2,2-triphenylvinyl)phenyl) methanimine (PITE1):

In a 50 mL round-bottom flask, **1** (1 eqv.) and **3** (1 eqv.) were refluxed in ethanol in presence of few drops of acetic acid for 6 h. After cooling the reaction mixture to room temperature an orange solid was obtained and filtered (yield 50%).

$^1\text{H NMR}$: δ_{H} (500 MHz, CDCl_3) 9.26 (1 H, dd, J 8.2, 1.4), 9.11 (1 H, s), 7.98 (1 H, d, J 8.8), 7.51 – 7.44 (1 H, m), 7.30 (1 H, s), 7.13 (13 H, dtt, J 7.7, 4.2, 2.1), 7.09 – 7.06 (1 H, m), 7.05 (4 H, d, J 1.8), 3.42 – 3.27 (2 H, m), 3.07 – 2.92 (2 H, m), 2.74 – 2.60 (4 H, m), 1.92 (2 H, q, J 7.8), 1.84 – 1.72 (2 H, m), 1.66 – 1.53 (4 H, m), 1.25 (3 H, t, J 7.3), 1.13 (6 H, td, J 7.3, 2.5), 1.04 (3 H, t, J 7.3).

$^{13}\text{C NMR}$: δ_{C} (126 MHz, CDCl_3) 156.06, 144.14, 144.13, 144.07, 141.06, 140.64, 140.17, 139.54, 139.53, 139.35, 138.79, 137.61, 133.72, 132.23, 131.56, 131.44, 131.42, 129.66, 127.91, 127.71, 127.58, 127.56, 126.32, 126.24, 126.18, 124.31, 123.31, 121.12, 120.23, 115.11, 103.86, 32.44, 31.83, 31.53, 30.84, 24.84, 24.37, 22.88, 21.33, 14.88, 14.75, 14.20, 13.88.

FTIR (frequency/ cm^{-1}): 3444 (broad), 2960, 1562, 1472, 1372, 1216, 698.

MS (MALDI-ToF): calculated for $\text{C}_{51}\text{H}_{52}\text{N}_2$ is 692.99 and found 693.892.

Synthesis of 6,7,8,9-tetrapropyl-2-(4-(1,2,2-triphenylvinyl) phenyl)pyrido[1,2-a]indole-10-carbaldehyde (PITE2):

A mixture of **2** (72 mg, 0.16 mmol) and **4** (75 mg, 0.16 mmol), K₂CO₃ (23 mg, 0.16 mmol), TBABr (5 mg, 0.015 mmol) and [Pd(PPh₃)₄] (5.6 mg, 0.005 mmol) was degassed. Then, water (1 mL) and toluene (10 mL) were added. The resulting mixture was stirred at 95°C for 24 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was quenched by adding water and extracted with dichloromethane. The organic layer was collected, dried over MgSO₄ and concentrated in vacuum. The product was purified by silica gel column chromatography (eluent: hexane/dichloromethane) to give the desired compound as light green solid in 68% yield (75 mg).

¹H NMR: δ_H (500 MHz, CDCl₃) 10.46 (1 H, s), 9.23 (1 H, d, *J* 1.8), 7.94 (1 H, d, *J* 9.1), 7.58 – 7.49 (3 H, m), 7.16 – 7.08 (15 H, m), 7.08 – 7.04 (2 H, m), 3.37 – 3.29 (2 H, m), 3.07 – 2.99 (2 H, m), 2.75 – 2.63 (4 H, m), 1.96 – 1.71 (4 H, m), 1.56 (4 H, d, *J* 6.2), 1.23 (3 H, t, *J* 7.3), 1.12 (9 H, q, *J* 7.1),

¹³C NMR: δ_C (126 MHz, CDCl₃) 184.20, 143.92, 143.83, 143.81, 143.76, 142.58, 140.96, 140.72, 139.58, 138.99, 138.13, 131.71, 131.47, 131.40, 131.35, 131.16, 130.88, 128.41, 127.80, 127.66, 127.61, 126.76, 126.54, 126.42, 126.33, 124.70, 121.16, 120.59, 115.57, 107.60, 32.77, 31.80, 31.75, 30.86, 24.78, 24.24, 22.21, 21.27, 14.92, 14.75, 14.32, 13.86.

FTIR (frequency/cm⁻¹): 3436 (broad), 2960, 2870, 1620, 1444, 698.

MS (MALDI-ToF): Calculated for C₅₁H₅₁NO is 693.98 and found 693.440.

II. Crystal structures

Instrumentation: Crystals of both **PITE1** and **PITE2** were grown from a mixture of ethyl acetate and ethanol through slow evaporation. Single-crystal X-ray diffraction data was collected using a Bruker APEX II diffractometer equipped with a CCD area detector using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) in phi(ϕ) and omega(ω) scan. The data collections for the **PITE1** and **PITE2** are obtained at 140 K and 150 K, respectively. The data collection was carried out giving an exposure time of 15 seconds per frame for **PITE1** and 10 seconds per frame for **PITE2** and at the crystal-to-detector distance of 6 cm. The data collection, unit cell measurements, integration, scaling and absorption corrections were done using Bruker Smart Apex II software.⁴ The intensity data was processed by using the Bruker SAINT Program suite.⁵ The crystal structures were refined by the full matrix least squares method using SHELXL97 present in the program suite WinGX (version 2014.1).^{6,7} Empirical absorption correction was applied using SADABS⁷ and the crystal packing diagrams were generated using Mercury 3.7 and Materials Studio 6.1. The detailed crystallographic data and the structure refinement parameters were summarized in **Table S1**.

The crystal structure investigation of **PITE1** reveals the strong Π - Π stacking interaction (3.29 \AA) responsible for fluorescence quenching. Such π - π stacking interaction (8.84 \AA) is absent in **PITE2**. In addition, the existence of a range of weak intramolecular interactions such as C-H... π and C-H...H-C are found to be responsible for restriction of intramolecular rotation in **PITE2** leading to strong fluorescence in the solid state. The short contacts in **PITE1** and **PITE2** are shown in Fig. S2 and indicated in Table S2. In the molecular structure of **PITE2**, there are 12 numbers of short contacts (C-H... π and C-H...H-C) involving TE unit compared to 8 such contacts in **PITE1**.

Table S1. Crystallographic data of **PITE1** and **PITE2**

Parameters	PITE1	PITE2
Empirical formula	C ₅₁ H ₅₂ N ₂	C ₅₁ H ₅₁ NO
Formula weight	692.95	693.93
Temperature	140 K	150 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 9.1338(2), b = 13.6605(2), c = 16.0445(3), α = 90.823(1), β = 91.397(1), γ = 101.432(1)	a = 10.4929(13), b = 11.1254(12), c = 16.981(2), α = 90.561(6), β = 96.469(7), γ = 99.986(6)
Volume	1961.23(6) Å ³	1939.0 (14) Å ³
Z	2	2
Density (calculated)	1.173 g/cc	1.189 g/cc
Absorption coefficient	0.067 mm ⁻¹	0.069 mm ⁻¹
F(000)	744.0	744.0
Crystal size	0.32 x 0.15 x 0.1 mm ³	0.25 x 0.21 x 0.12 mm ³
Theta range for data collection	1.3 to 30.3°	2.0 to 24.7°
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19
Reflections collected	43653	38957
No. of unique ref./ obs. Ref.	11623/ 6311	6599/ 4036
Data completeness	99.2%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.993 and 0.980	0.993 and 0.980
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
parameters	482	483
Goodness-of-fit on F²	1.048	1.001
Final R indices [I > 2σ_I]	R1 = 0.0577, wR2 = 0.119	R1 = 0.0580, wR2 = 0.148
R indices (all data)	R1 = 0.122, wR2 = 0.1480	R1 = 0.114, wR2 = 0.1820
Largest diff. peak and hole	0.228 and -0.286 e.Å ⁻³	0.309 and -0.239 e.Å ⁻³
CCDC Number	CCDC 1442235	CCDC 1442108

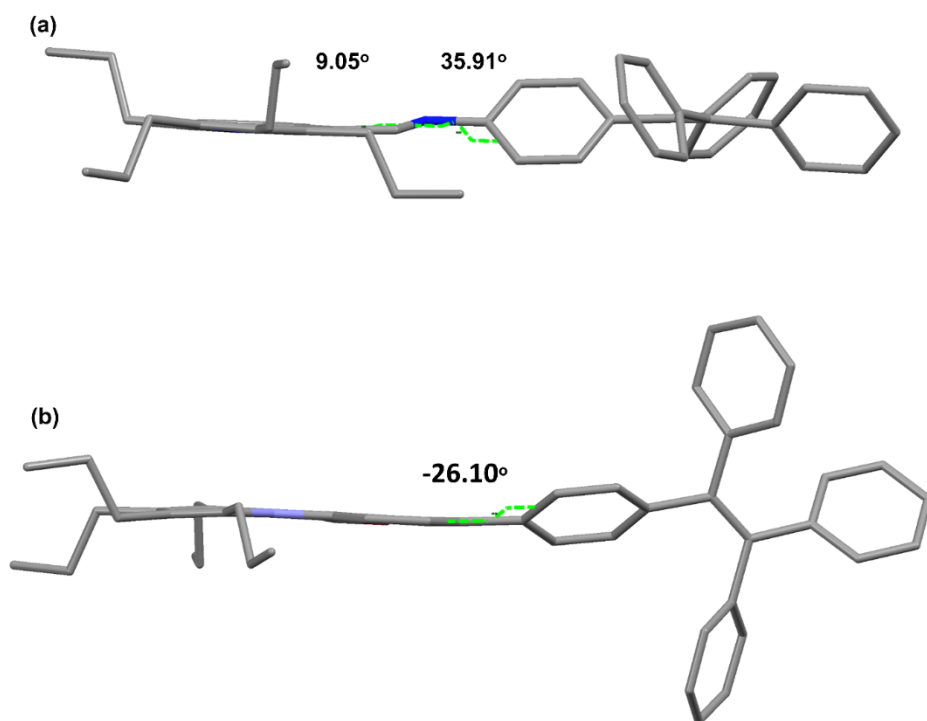


Fig. S1. (a) The angle between the planar PI part and the directly linked phenyl ring of the TE unit through the imine bridge in **PITE1** is 44.96° . (b) The torsion angle between PI and TE unit in **PITE2** is -26.10° .

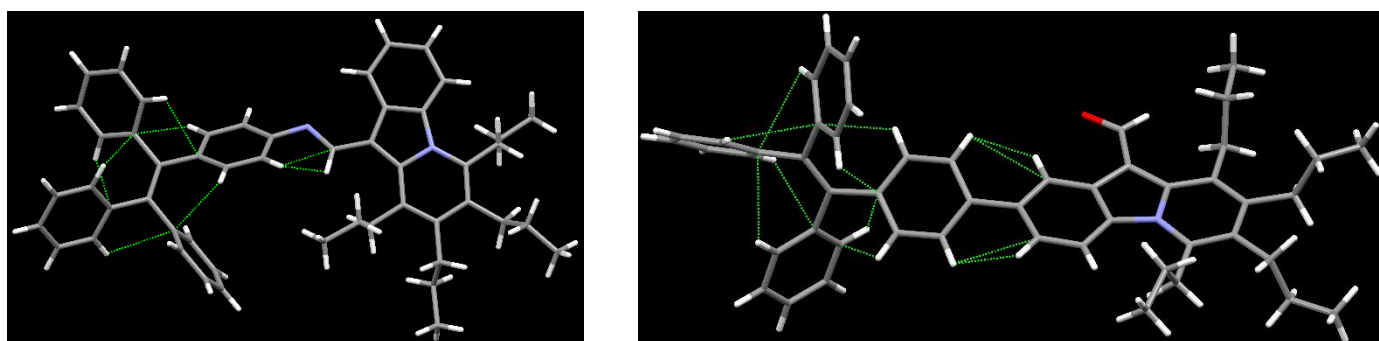


Fig. S2. The molecular structures obtained from crystal structure investigations of (a) **PITE1** and (b) **PITE2** showing the intramolecular interactions involving TE unit.

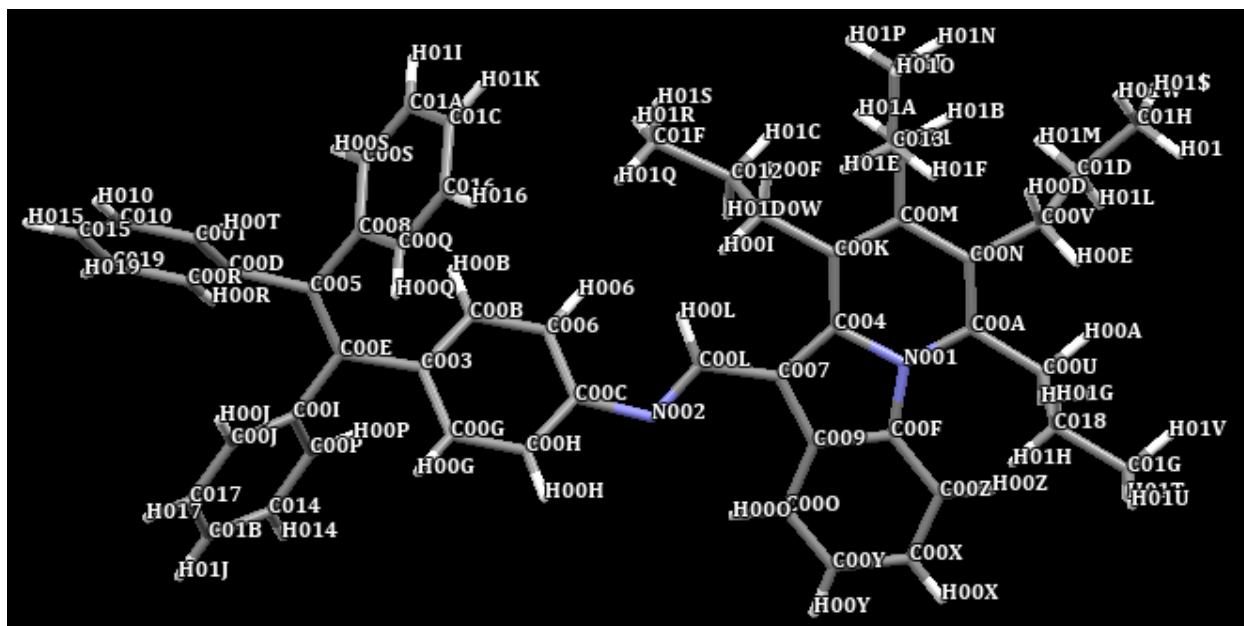


Fig S3. Molecular structure of **PITE1** from single crystal X-ray analysis with labeling the atoms.

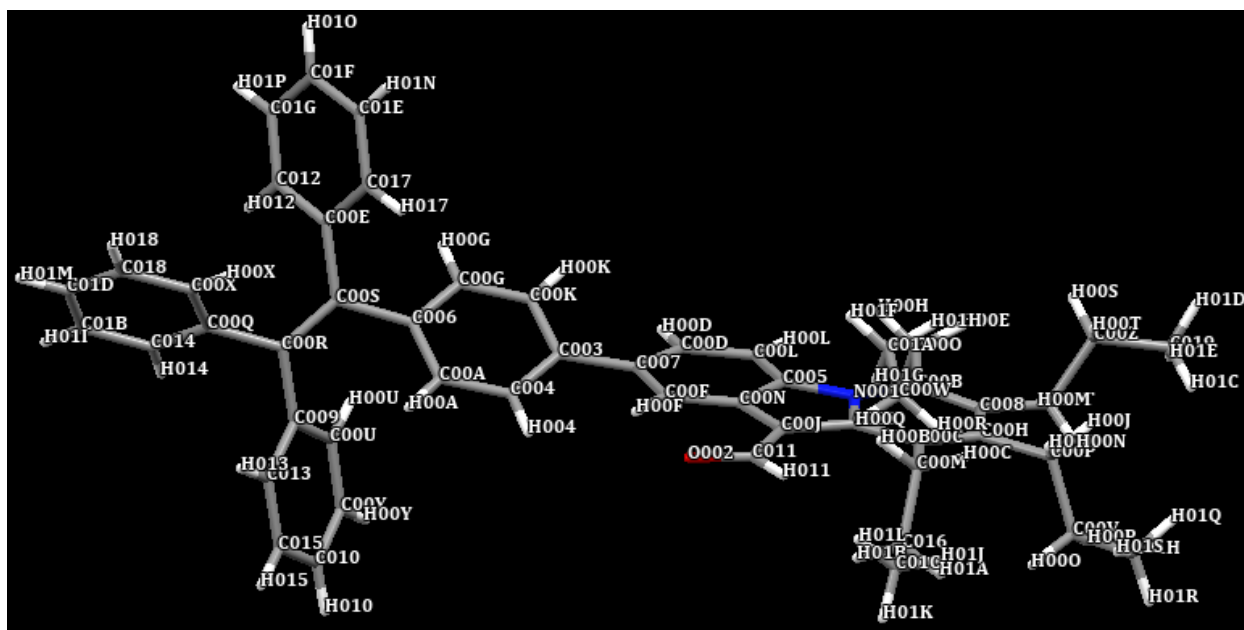


Fig S4. Molecular structure of **PITE2** from single crystal X-ray analysis with labeling the atoms.

Table S2. The intramolecular interactions (C–H...H–C, C–H... π) in **PITE1** and **PITE2** involving TE unit.

Number	Intramolecular interactions in PITE2			Intramolecular interactions in PITE1		
	Atom1	Atom2	Length (Å)	Atom1	Atom2	Length (Å)
1	H017	C006	2.753	H00G	C00I	2.745
2	H00G	C017	3.109	H00P	C003	2.732
3	C00E	H00X	2.763	H00B	C008	2.709
4	H00A	C009	2.768	C008	H00T	2.713
5	H00U	C006	2.855	H00J	C00D	2.795
6	C00Q	H013	2.857	H00R	C00I	2.751
7	C009	H014	2.808	H006	C00L	2.693
8	C00Q	H012	2.765	H006	H00L	2.205
9	H004	C00F	2.691			
10	H00F	H004	2.170			
11	H00D	H00K	2.248			
12	H00K	C00D	2.721			

III. Spectroscopic data

Instrumentation: The UV-Vis absorption spectra were recorded on a Cary 100 spectrophotometer. Steady-state fluorescence measurements were carried out on a Jobin Yvon Horiba Model Fluorolog-3-21. Time-resolved fluorescence measurements were carried out using time-correlated single-photon counting (TCSPC) spectrometer (Delta Flex-01-DD/HORIBA). Delta diode laser 408 nm with FWHM = 198 ps was used as excitation source. Picosecond photon detection module with photomultiplier tube was used as detector. Instrument response function was recorded by using aqueous solution of Ludox. Decay curves were analyzed by nonlinear least-squares iteration using IBH DAS6 (version 6.8) decay analysis software.

Fluorescence quantum yield (Φ_f) measurement:

The fluorescence quantum yields of **PITE1** and **PITE2** in different solvents and aqueous dispersion of nanoparticles were estimated by comparison with coumarin-153 in ethanol ($\Phi_f = 0.53$).⁸ The quantum yields were calculated using the following equation.⁹

$$\Phi_{f,x} = \Phi_{f,s} \cdot \frac{F_x}{F_s} \cdot \frac{f_s}{f_x} \cdot \frac{n_x^2}{n_s^2}$$

where, Φ_f is fluorescence quantum yield, subscript x denotes unknown sample and subscript s refers to standard. F denotes integral fluorescence, n refers to refractive index of the solvent used in the measurements and f is the absorption factor at the excitation wavelength given by the following equation:

$f = 1 - 10^{-\varepsilon(\lambda_{ex})cl} = 1 - 10^{-A(\lambda_{ex})}$, where A is absorbance and ε = molar extinction coefficient in $\text{L mol}^{-1} \text{cm}^{-1}$.

The fluorescence quantum yield of **PITE2** powder was estimated using a calibrated integrating sphere (Quanta-Phi, Horiba).

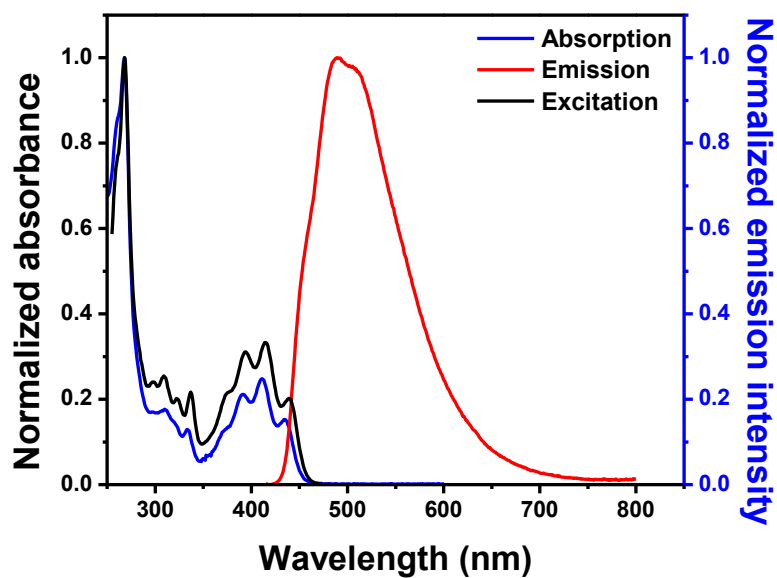


Fig. S5. Normalized absorption, emission ($\lambda_{\text{ex}} = 410$ nm) and excitation ($\lambda_{\text{em}} = 480$ nm) spectra of unsubstituted pyrido[1,2-a]indole (**1**).

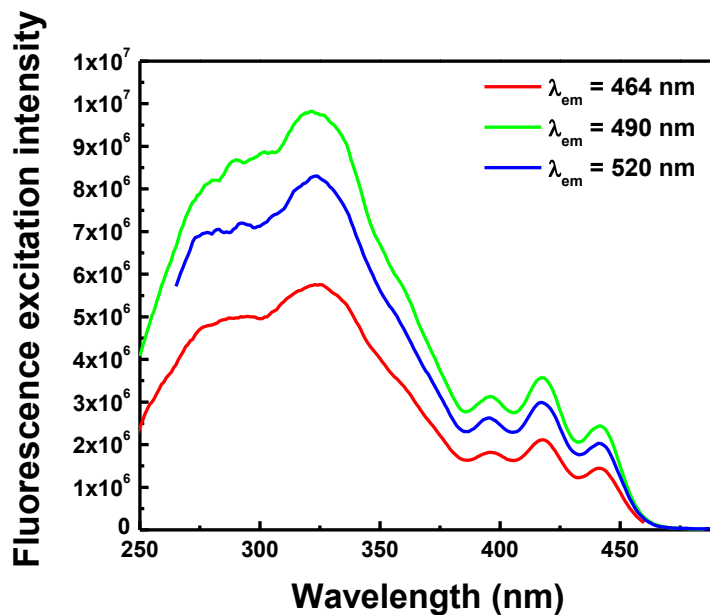


Fig. S6. Excitation spectra of **PITE2** in THF monitoring at different emission wavelengths resemble to absorption spectra.

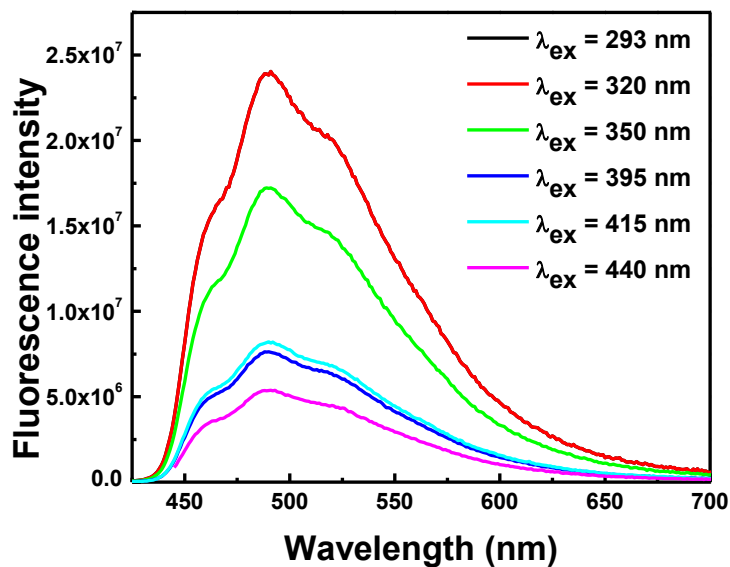


Fig S7. Emission spectra of **PITE2** in THF exciting at different wavelengths.

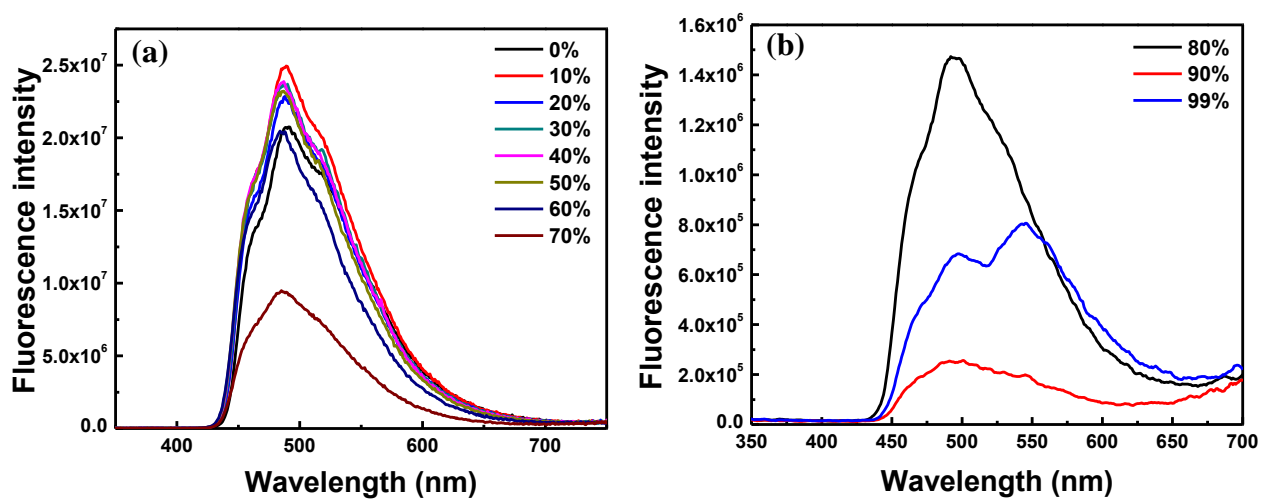


Fig. S8. (a, b) Emission ($\lambda_{\text{ex}} = 320 \text{ nm}$) spectra of **PITE2** in different THF-water composition with increasing water fraction.

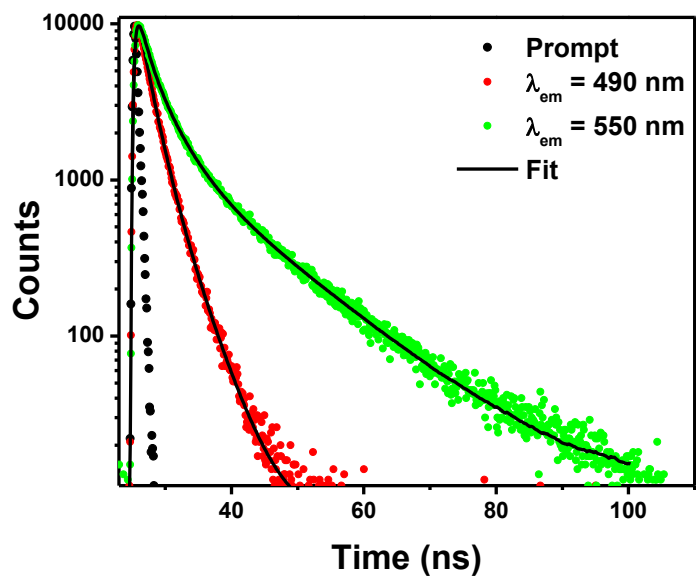


Fig. S9. Decay profiles of aqueous dispersion of nanoparticles ($\lambda_{ex} = 408$ nm). The continuous black lines are the exponential fit to the decay curves.

Table S3. Spectroscopic data of **PITE2** in various organic solvents; lifetime (τ) and the quality of fitting (χ^2) for the data in Fig. 4d (in main text) are shown.

Solvent		Absorption		Fluorescence		Lifetime (ns) $\lambda_{em} = 490$ nm	
Entry	E_T30^{10}	λ_{max} (nm) TE region	λ_{max} (nm) PI region	λ_{max} (nm)	Quantum yield (%)	$\lambda_{ex} = 340$ nm (χ^2)	$\lambda_{ex} = 410$ nm (χ^2)
Toluene	0.099	320	419	493	50	8.1 (1.02)	8.1 (1.11)
Tetrahydrofuran	0.207	318	417	490	54	9.0 (1.04)	9.1 (1.05)
Chloroform	0.259	321	414	490	49	7.2 (1.09)	7.3 (1.2)
Acetonitrile	0.460	313	413	487	48	7.8 (1.05)	7.8 (1.10)

Table S4. Spectroscopic data of **PITE2** nanoparticles and solid; the weighted average lifetime (τ_{avg}) and the quality of fitting (χ^2) for the data in Fig. S6 are shown.

Entry	Absorption		Fluorescence		Lifetime (ns) $\lambda_{ex} = 410$ nm	
	λ_{max} (nm) TE region	λ_{max} (nm) PI region	λ_{max} (nm)	Quantum yield (%)	$\lambda_{em} = 495$ nm (χ^2)	$\lambda_{em} = 548$ nm (χ^2)
Aqueous dispersion of nanoparticles	320	419	495, 548	8.5	7.0 (1.0)	2.5 (1.09)
Solid powder	322	417	493, 546	20	----	----

IV. Future prospects of PITE1 and PITE2

The presence of imine bond in **PITE1** leads to the quenching of fluorescence in the solution state due to the photoinduced electron transfer (PeT) processes. The addition of thiol-containing compounds like cysteine and homocysteine to the solution of **PITE1** leads to the cleavage of imine bond. Subsequently, the fluorescence of the pyridoindole moiety observed demonstrating **PITE1** as a prospective ‘turn-on’ fluorescent sensor (Fig. S10, S11).

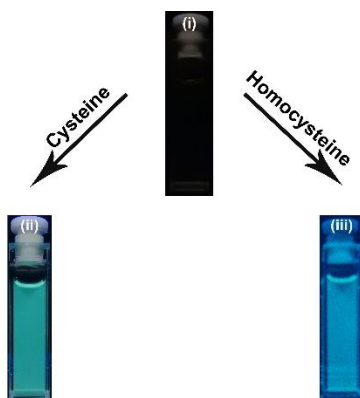


Fig. S10. Images under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) of (i) $5 \mu\text{M}$ **PITE1** in THF, (ii) $5 \mu\text{M}$ **PITE1** with 3 mM L-cysteine and (iii) $5 \mu\text{M}$ **PITE1** with 1.6 mM homocysteine.

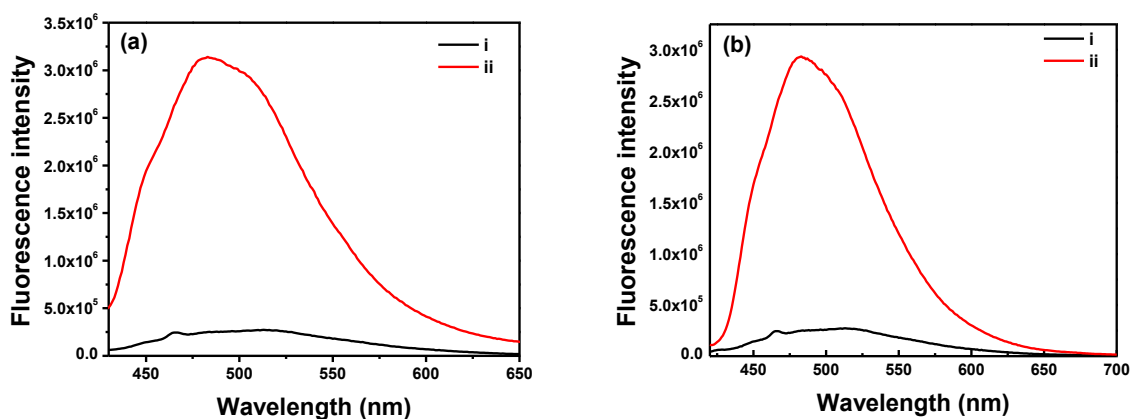


Fig. S11. Emission spectra ($\lambda_{\text{ex}} = 410 \text{ nm}$) of (a) **PITE1** with L-cysteine and (b) **PITE1** with homocysteine: (i) $5 \mu\text{M}$ THF solution of **PITE1** and (ii) the solution of **PITE1** with the corresponding thiol.

The addition of trifluoroacetic acid (TFA) to the solution of **PITE2** completely quench the fluorescence and subsequent addition of triethylamine (TEA) leads to the regaining of fluorescence (Fig. S12, S13).

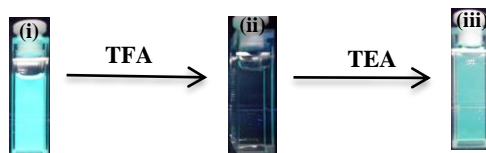


Fig. S12. Images under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) of $5 \mu\text{M}$ **PITE2** in (i) Chloroform, after adding (ii) TFA and (iii) TEA.

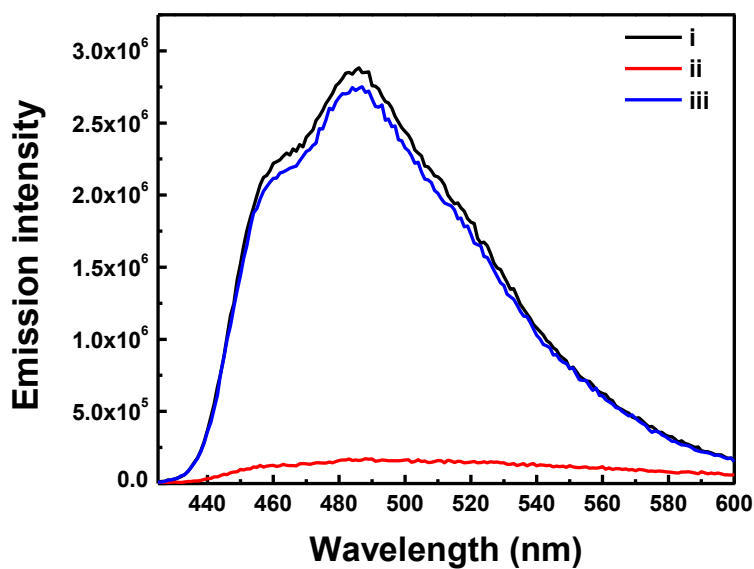


Fig S13. Emission spectra of $5 \mu\text{M}$ solution of **PITE2** in (i) Chloroform, (ii) Chloroform + $10 \mu\text{L}$ TFA and (iii) addition of $10 \mu\text{L}$ TEA in (ii).

IV. References

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FTIR Spectra

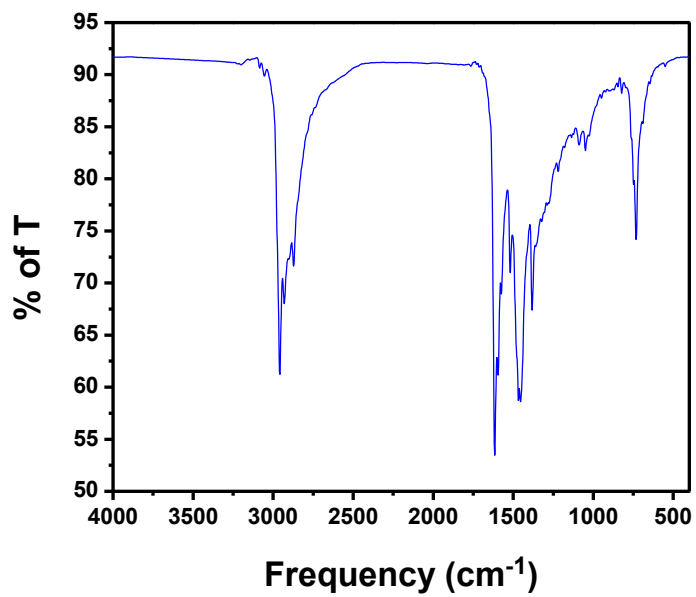


Fig S14. FTIR Spectrum of compound 1.

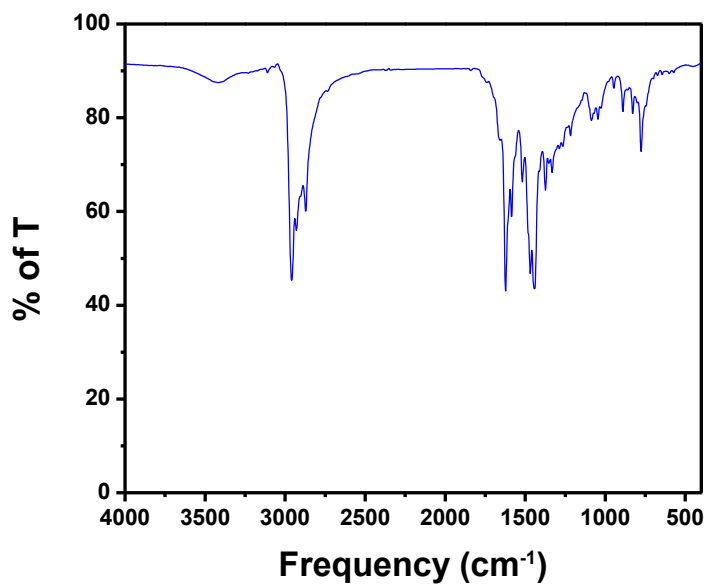


Fig S15. FTIR Spectrum of compound 2.

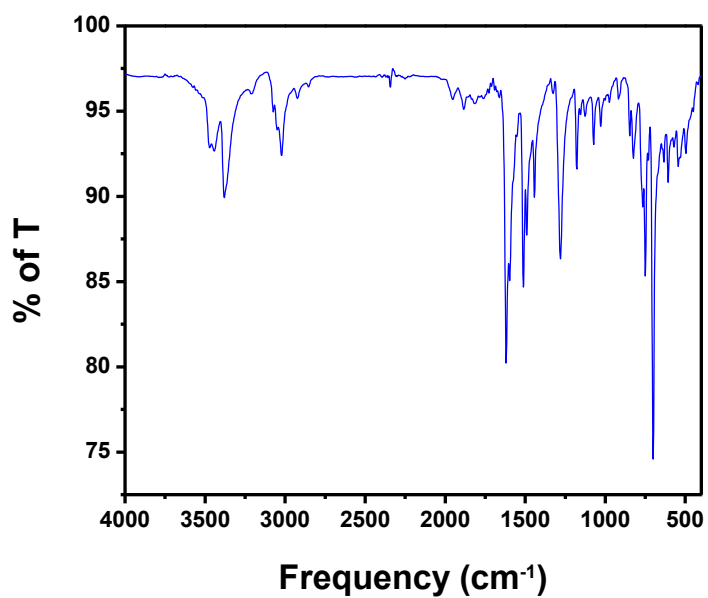


Fig S16. FTIR Spectrum of compound **3**.

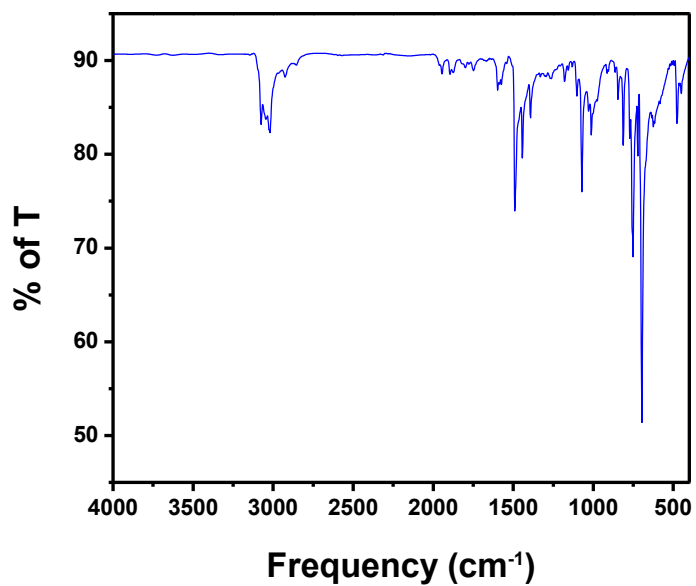


Fig S17. FTIR Spectrum of compound **3a**.

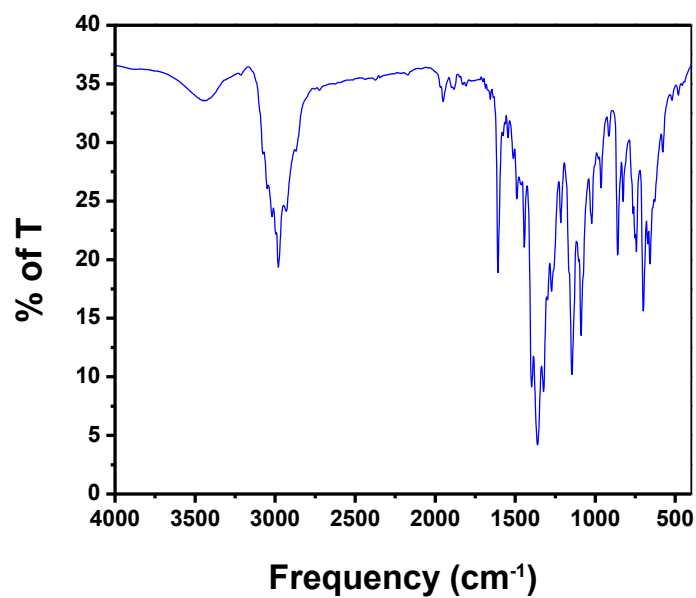


Fig S18. FTIR Spectrum of compound **4**.

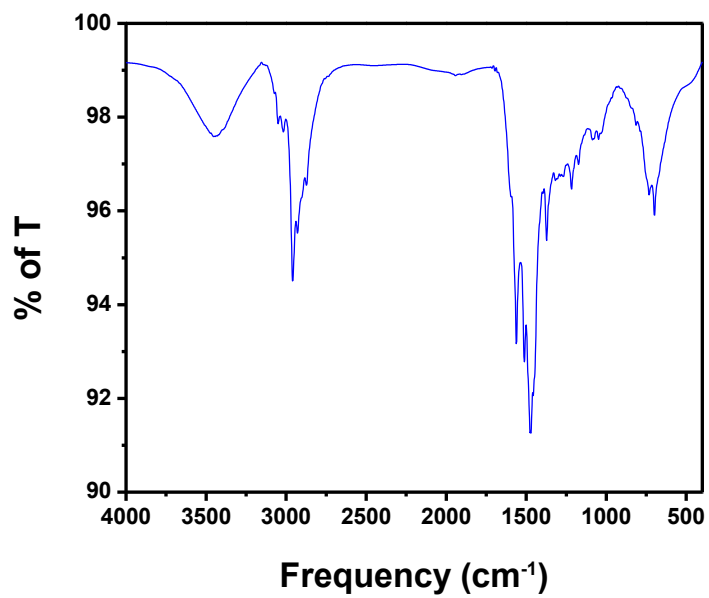


Fig S19. FTIR Spectrum of **PITE1**.

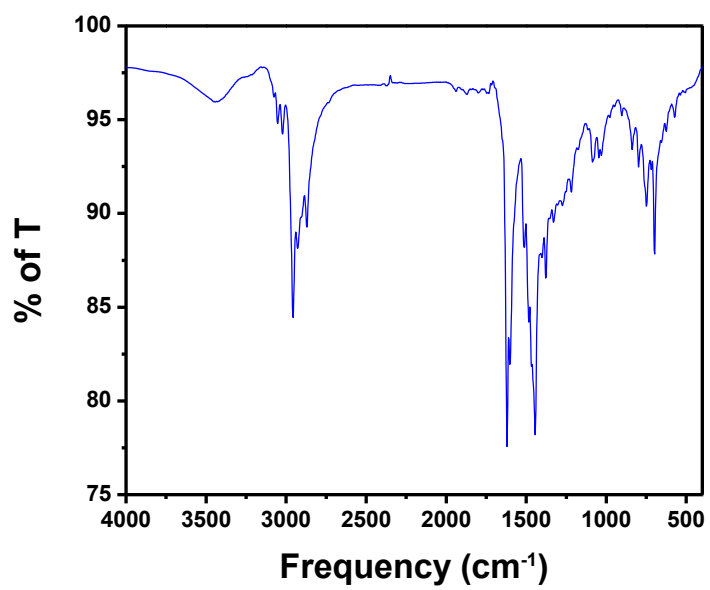


Fig S20. FTIR Spectrum of **PITE2**.

^1H NMR spectra

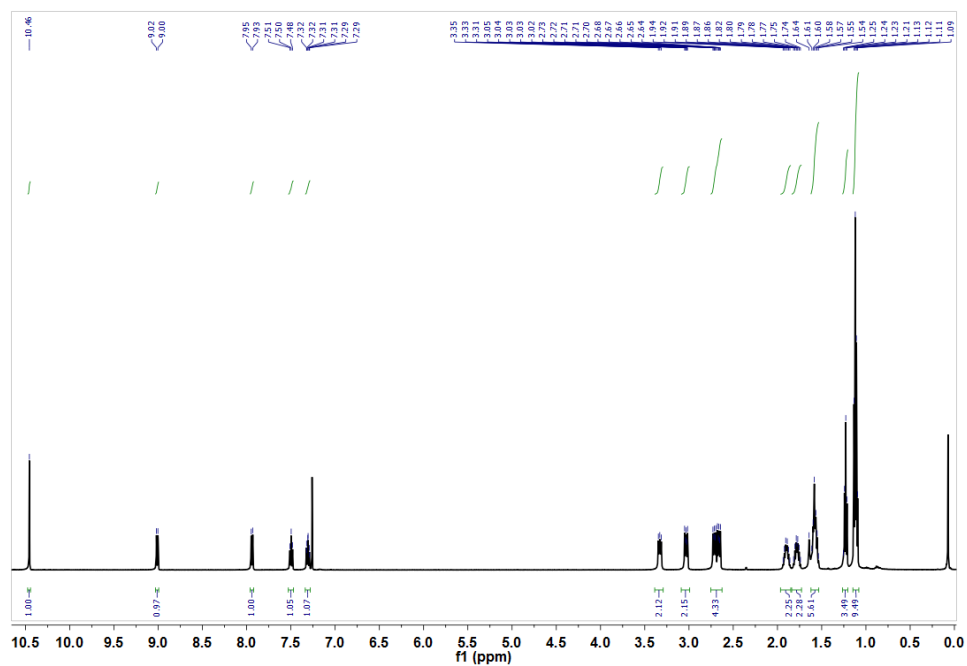


Fig S21. ^1H NMR spectrum of 1.

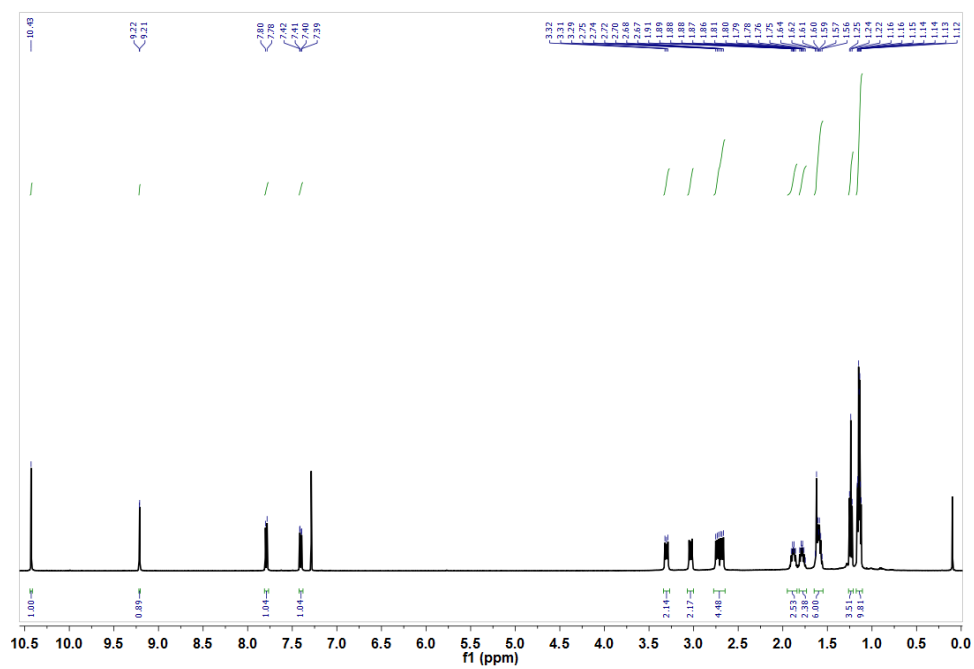


Fig S22. ^1H NMR spectrum of 2.

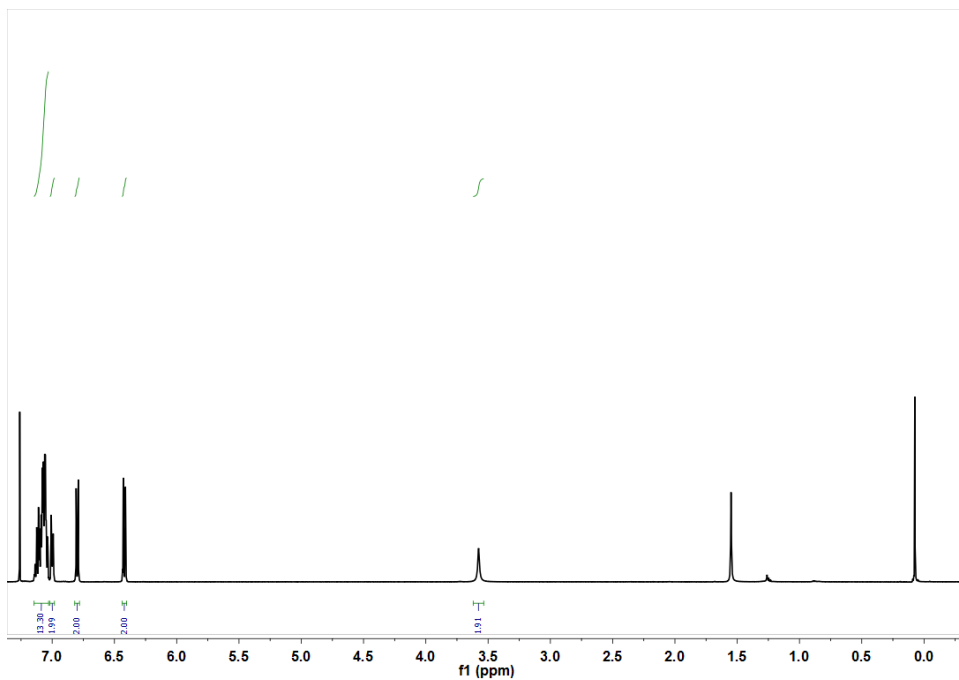


Fig S23. ¹H NMR spectrum of **3**.

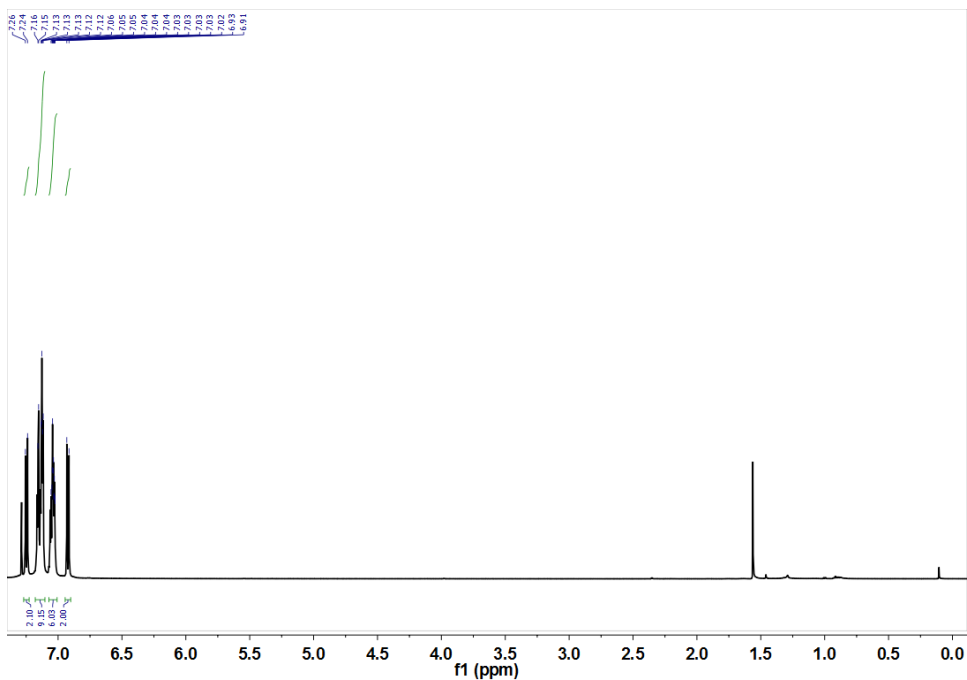


Fig S24. ¹H NMR spectrum of **3a**.

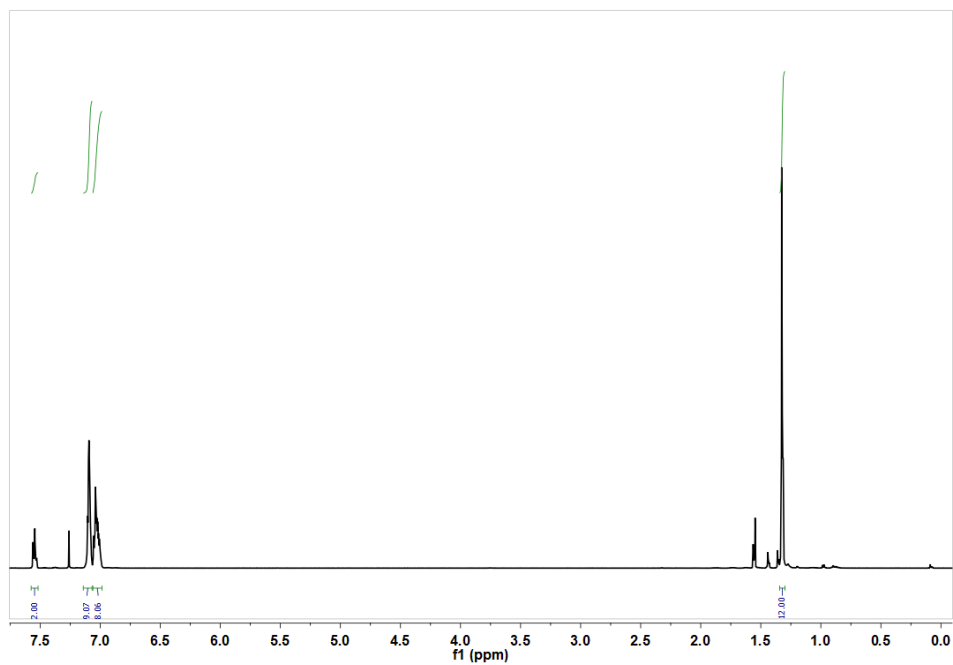


Fig S25. ^1H NMR spectrum of **4**.

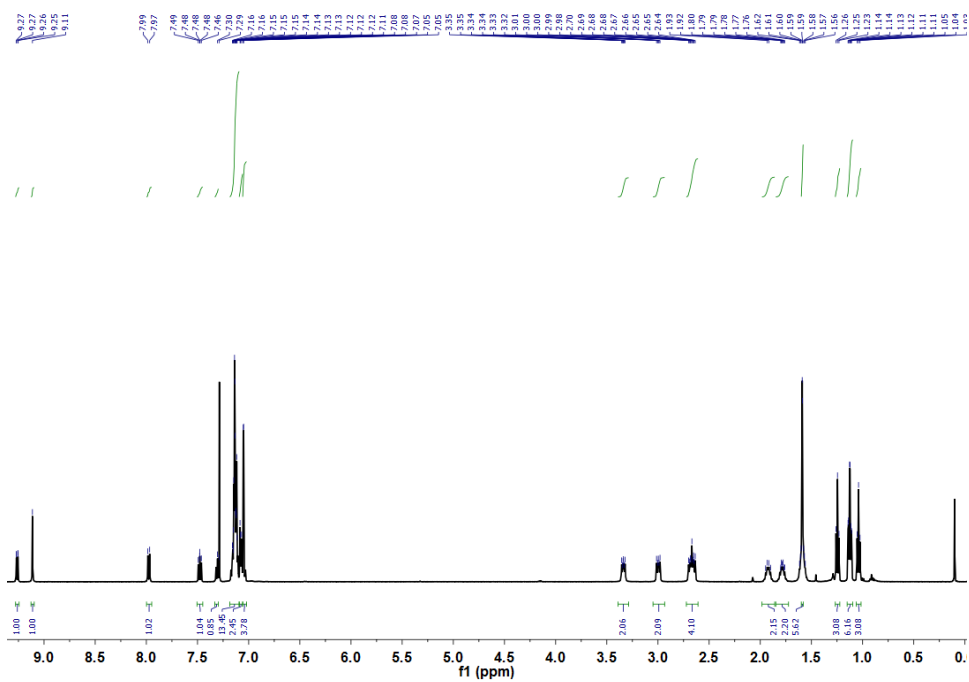


Fig S26. ¹H NMR spectrum of PITE1.

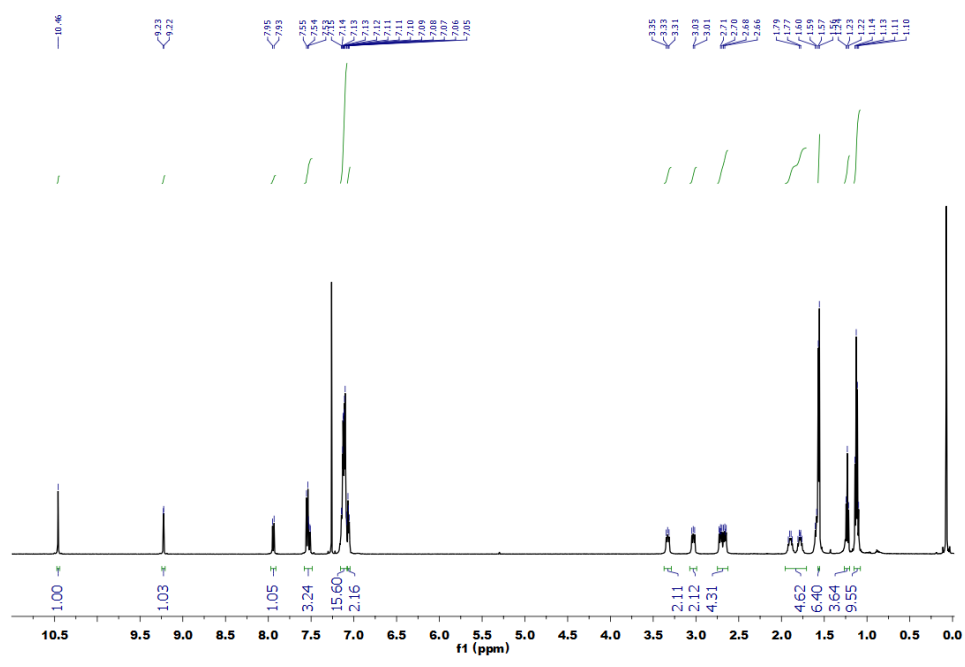


Fig S27 ¹H NMR spectrum of PITE2.

^{13}C NMR spectra

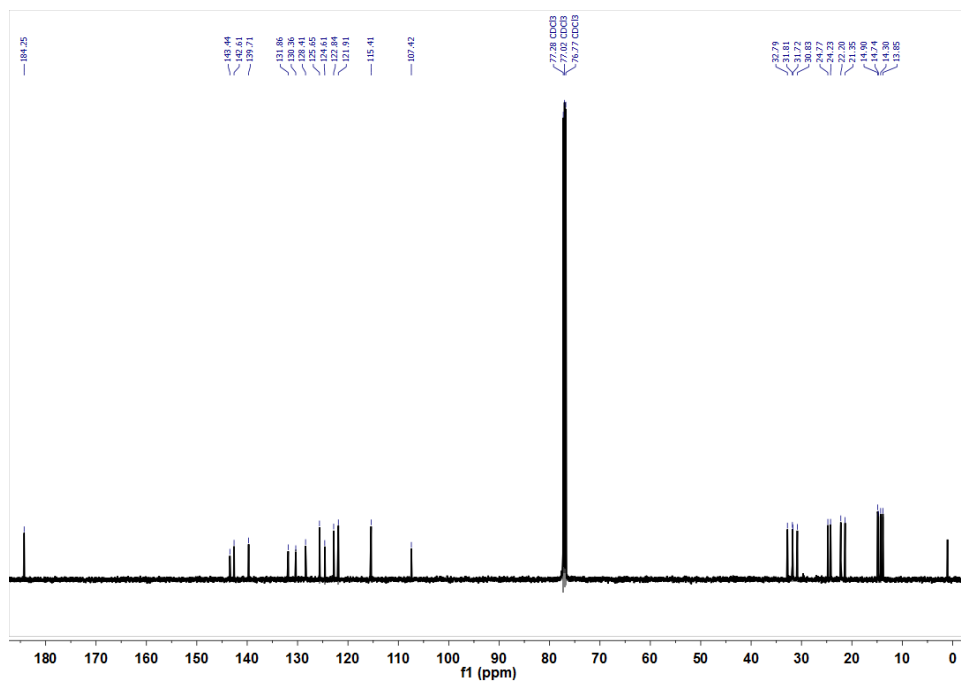


Fig S28. ^{13}C NMR spectrum of 1.

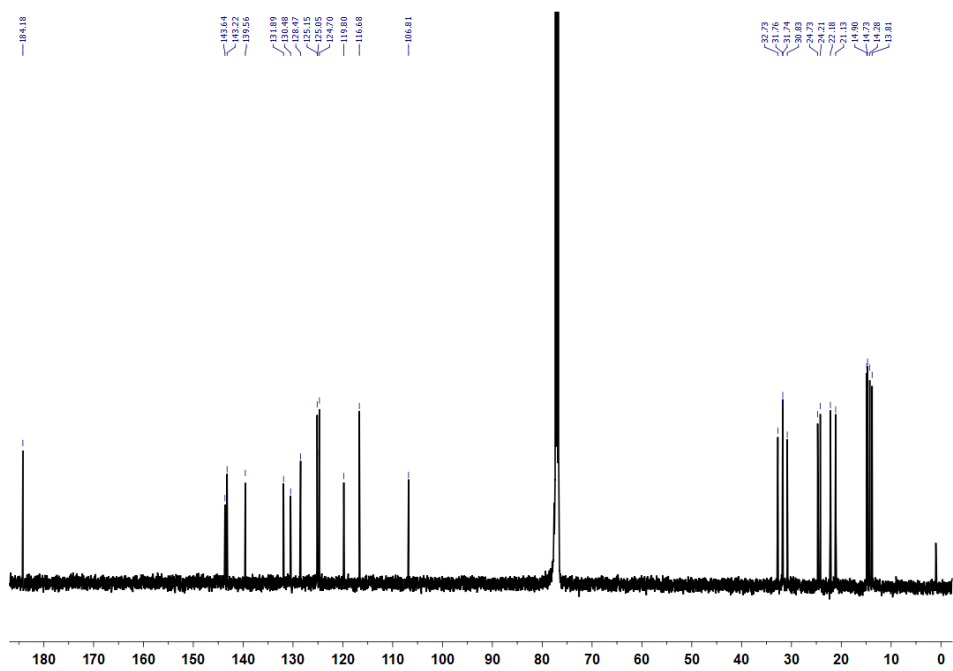


Fig S29. ^{13}C NMR spectrum of 2.

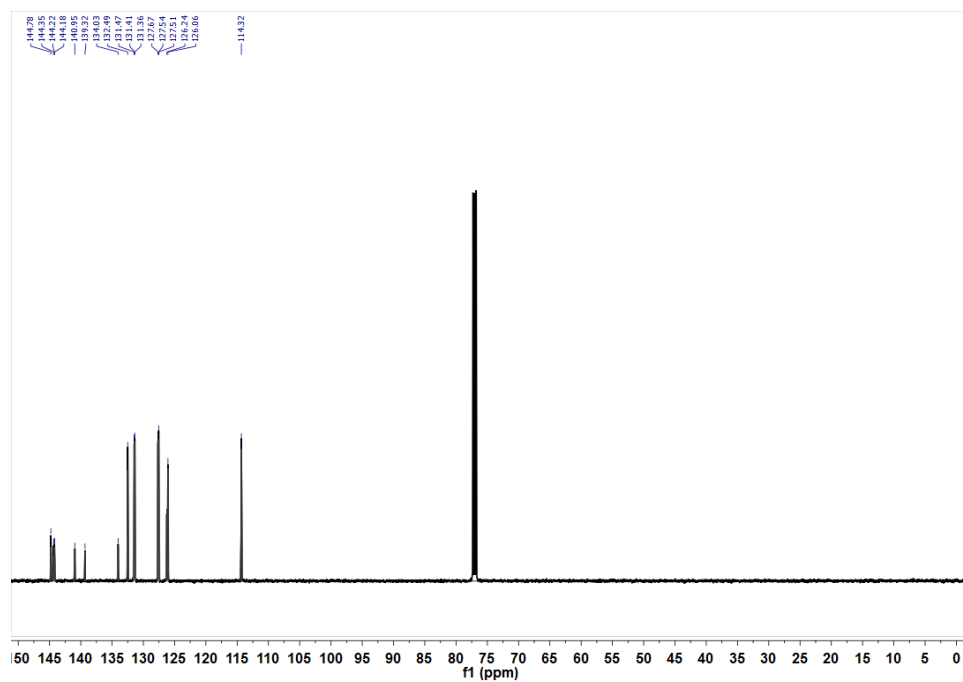


Fig S30. ^{13}C NMR spectrum of **3**.

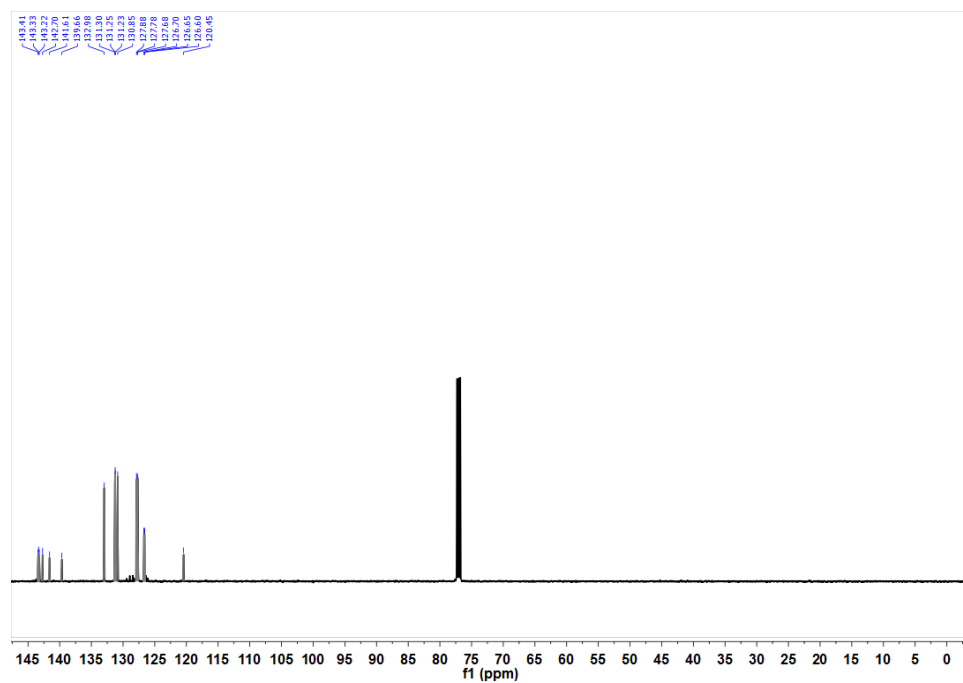


Fig S31. ^{13}C NMR spectrum of **3a**.

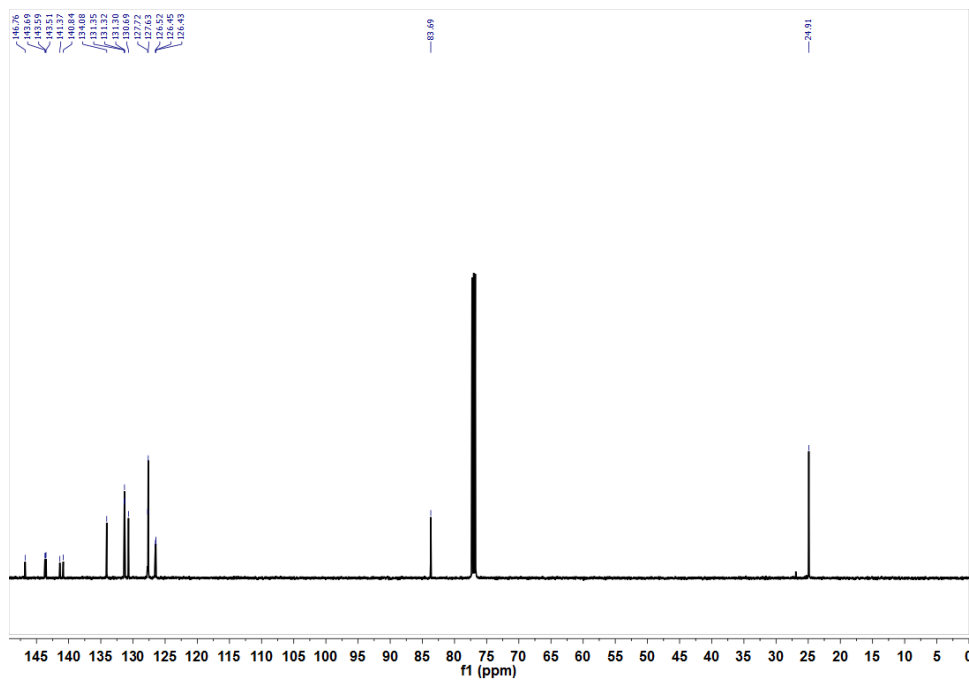


Fig S32. ^{13}C NMR spectrum of **4**.

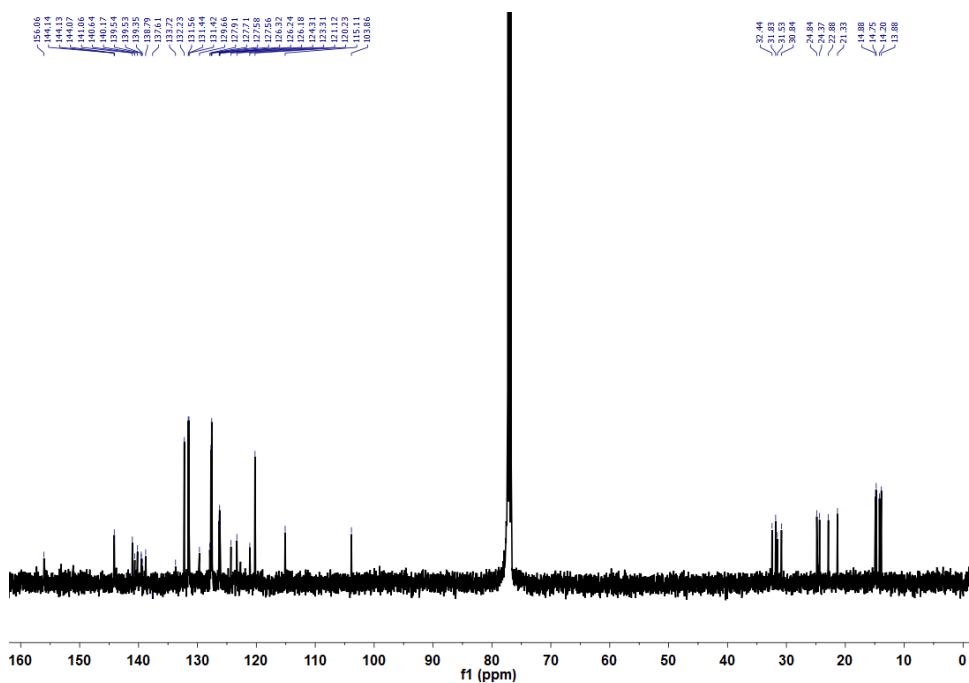


Fig S33. ^{13}C NMR spectrum of **PITE1**.

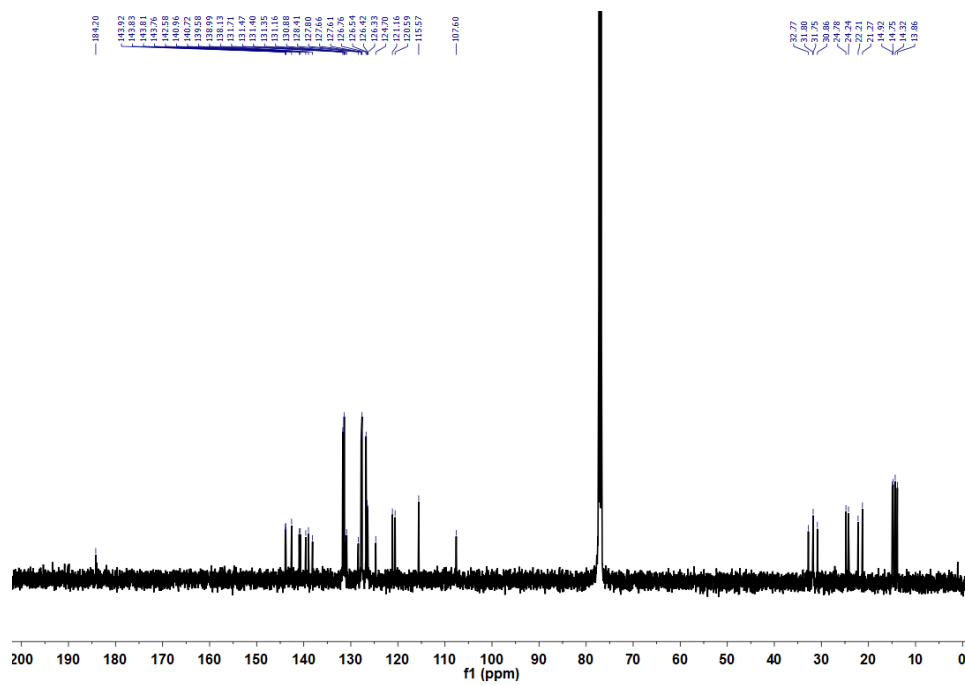


Fig S34. ^{13}C NMR spectrum of PITE2.