Supplementary Information

Aggregation-Induced Enhanced Emission (AIEE), pH Sensing and Selective Detection of Sulfuric Acid of Novel Imidazole-Based Surrogates Made via Microwave-Assisted Synthesis

Noorullah Baig[a,b], Suchetha Shetty[a,b], Anuvasita Parikh[c], Ajay K. Sah[c], Bassam Alameddine[*a,b]

[a] Department of Mathematics and Natural Sciences, Gulf University for Science and Technology, Mubarak Al-Abdullah, Hawally 32093, Kuwait.

[b] Functional Materials Group, Gulf University for Science and Technology, Mubarak Al-Abdullah, Hawally 32093, Kuwait.

[c] Department of Chemistry, Birla Institute of Technology and Science, Pilani; Pilani Campus, Rajasthan 333031, India.

*†Correspondence: *E-mail address*: alameddine.b@gust.edu.kw; Tel: +965 2530 7476

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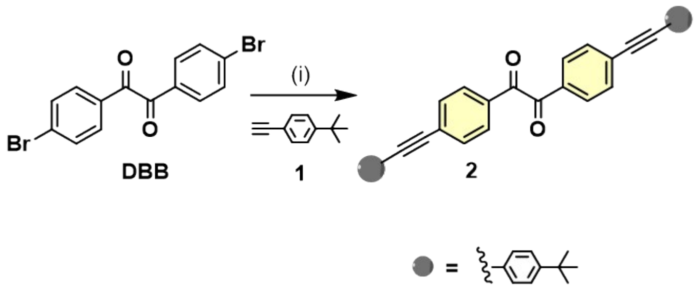
Experimental section

EXPERIMENTAL SECTION

General Information

All reactions were conducted under dry argon and the reagents were acquired from Merck (Darmstadt, Germany), HiMedia (Mumbai, India) and CDH (Delhi, India) and employed as purchased without any further purification, except where noted otherwise. The synthesis of 1,2-bis(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)ethane-1,2-dione (**2**) followed previously established procedures.[1,2] All the organic solvents employed in the reactions and purification steps were dried over molecular sieves and deoxygenated by purging with argon gas for 30 minutes prior to use. Thin-layer chromatography (TLC) was performed on Al sheets coated with silica gel 60 F254 and visualized under a UV lamp. Nuclear Magnetic Resonance spectra, including ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz), were recorded using a Bruker Avance III spectrometer at 25°C. $CDCl_3$ served as the solvent, and chemical shifts (δ) were reported in parts per million (ppm), referenced to tetramethylsilane (TMS). Electrospray ionization high-resolution mass spectra (ESI-HRMS) were acquired on an Agilent 6545 LC-QTOF system. The XRD patterns were obtained using a RIGAKU MINIFLEX II X-ray diffractometer with a Cu K X-ray source (λ= 1.542 Ǻ) and a scanning rate 2°/min. Particle size was analyzed using Anton Paar particle size analyzer. A Horiba Delta Flex 01 was used for fluorescence lifetime measurements using a time-correlated single-photon counting (TCSPC) method. The sample was excited using a laser diode at 365 nm. UV-Vis spectra were recorded on a Shimadzu UV1800 spectrophotometer. Photoluminescence (PL) spectra were obtained using an Agilent G9800 Cary Eclipse Fluorescence spectrophotometer. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded on the Shimadzu IRAffinity-1S system. Spectra were recorded using fine grinded powder of sample on Attenuated Total Reflection (ATR) setup.

Synthetic procedure



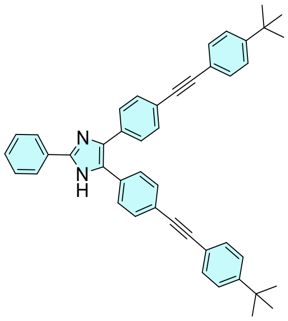
Reagents and reaction conditions:
(i) $Pd_2(dba)_3$, CuI, iPr_2NH, PPh_3, 90ºC, 2 days.

Scheme S1: Synthesis of 2

1,2-bis(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)ethane-1,2-dione ***2*** *(procedure A)*

A Schlenk tube was charged under an inert atmosphere of argon with 1,2-bis(4-bromophenyl)ethane-1,2-dione **DBB** (1.0 g, 2.75 mmol, 1 eq.), 4-tert-Butylphenylacetylene **1** (2.33 mL, 12.9 mmol, 4.7 eq), $[Pd_2(dba)_3]$ (30 mg, 0.03 mmol, 12 mol%), PPh_3 (17 mg, 0.06 mmol), and CuI (12.5 mg, 0.06 mmol) in 5 mL of degassed diisopropylamine (iPr_2NH) and the solution was refluxed for 2 days. The resulting residue was extracted with DCM/$NaHCO_3$, and the organic layer was washed with a brine solution followed by deionized water (100 mL × 3). The desired product was isolated by silica gel column chromatography, using pure hexane as eluent. Yellow solid (1.3 g, 90%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.0 (d, 4H, J = 8.7 Hz,), 7.68 (d, 4H, J = 8.8 Hz,), 7.53 (d, 4H, J = 8.6 Hz,), 7.43 (d, 4H, J = 8.8 Hz,), 1.36 (s, 18H,). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 193.3, 152.5, 132.0, 131.7, 131.6, 130.5, 129.8, 125.5, 119.3, 94.5, 87.9, 34.9, 31.1. EI-HRMS: m/z calculated for $M^{\bullet+}$ $C_{38}H_{34}O_2$ 522.2559 found 522.2568. FTIR (KBr, cm^{-1}): 2950 (C-H str), 2205 (C≡C str), 1655 (C=O str), 1595 (C=C str), 1163 (C=O ben), 832 (C-H ben).

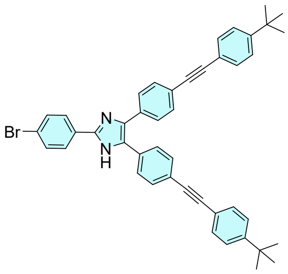
*4,5-bis(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)-2-phenyl-1H-imidazole (**4a**) (procedure B)*



4a

To a microwave reactor containing **2** (0.16 g, 0.37 mmol, 1 eq.) in 3.0 mL of degassed acetic acid, benzaldehyde **3a** (0.03 mL, 0.3 mmol, 1 eq.) and ammonium acetate (0.231 g, 3.0 mmol, 10 eq.) were added. The reaction mixture underwent heating at 180 °C for 10 minutes under a nitrogen atmosphere and the resultant yellow suspension dissolved in DCM and extracted with a saturated solution of $NaHCO_3$ (25 mL x 2). The combined organic layer was washed with deionized water (25 mL × 3), concentrated, and the product was purified by silica gel column chromatography using DCM/hexane (30:80 v/v) as eluent Affording a yellow solid (162 mg, 89%).^{1}H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.95 (*d*, 2H, J = 6.9 Hz,), 7.53-7.46 (*m*, 14H,), 7.44-7.39 (*m*, 5H,), 1.35 (*s*, 18H,). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 151.6, 146.6, 131.9, 131.3, 129.6, 129.0, 128.9, 127.6, 125.4, 125.3, 120.1, 88.6, 34.8, 31.2, EI-HRMS: m/z calculated for $M^{\bullet+}$ $C_{45}H_{40}N_2$ 608.3191 found 608.3180. FTIR (KBr, cm^{-1}): 2955 (C-H str), 1514 (C=C str), 1102 (C-N str), 832 (C-H ben).

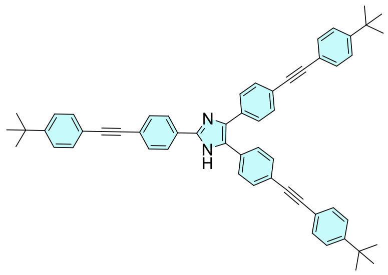
*2-(4-bromophenyl)-4,5-bis(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)-1H-imidazole **4b***



4b

4b was prepared following procedure B with: 4-Bromobenzaldehyde **3b** (74 mg, 0.4 mmol, 1 eq.), **2** (208 mg, 0.4 mmol, 1 eq.), and ammonium acetate (308 mg, 4.0 mmol, 10 eq.). Yellow solid (260 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.78 (*d*, 2H, J = 8.6 Hz,), 7.60 (*d*, 3H, J = 8.6 Hz,), 7.53-7.49 (*m*, 10H,), 7.41(*d*, 5H, J = 8.6 Hz,), 1.35 (*s*, 18H,). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 151.6, 145.5, 132.1, 131.9, 131.3, 128.5, 127.6, 126.8, 125.4, 123.1, 120.1, 88.6, 34.8, 31.2, EI-HRMS: m/z calculated for $M^{\bullet+}$ $C_{45}H_{39}BrN_2$ 688.2276 found 688.2234. FTIR (KBr, cm^{-1}): 2951 (C-H str), 2219 (C≡C str), 1488 (C=C str), 1102 (C-N str), 832 (C-H ben).

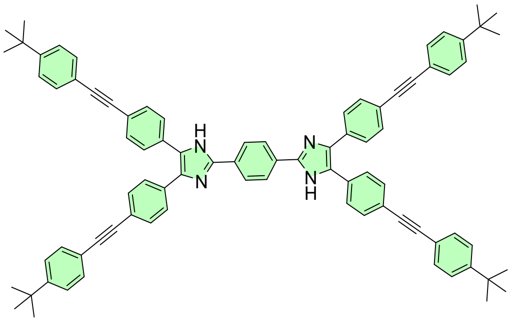
2,4,5-tris(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)-1H-imidazole ***4c***



4c

4c was prepared following procedure A with: **4b** (150 mg, 0.22 mmol, 1 eq.), 4-tert-Butylphenylacetylene **1** (0.094 mL, 0.52 mmol, 2.4 eq), [$Pd_2(dba)_3$] (1.2 mg, 0.001 mmol, 6 mol%), PPh_3 (0.6 mg, 0.002 mmol), and CuI (0.5 mg, 0.002 mmol). Yellow solid (146 mg, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.90 (*d*, 2H, J = 8.4 Hz,), 7.67-7.50 (*m*, 15H,), 7.42-7.40 (*m*, 8H,), 1.36 (*s*, 27H,). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 151.8, 132.1, 131.5, 131.4, 131.3, 127.6, 126.9, 125.4, 125.2, 119.9, 88.3, 34.8, 31.1, EI-HRMS: m/z calculated for $M^{\bullet+}$ $C_{57}H_{52}N_2$ 764.4130 found 764.4135. FTIR (KBr, cm^{-1}): 2958 (C-H str), 2000 (C≡C str), 1507 (C=C str), 1105 (C-N str), 836 (C-H ben).

1,4-bis(4,5-bis(4-((4-(tert-butyl)phenyl)ethynyl)phenyl)-1H-imidazol-2-yl)benzene ***4d***



4d

4d was prepared following procedure B with: Terephthalaldehyde **3c** (16.7 mg, 0.12 mmol, 1 eq.), **2** (130 mg, 0.25 mmol, 2 eq.), and ammonium acetate (96 mg, 1.2 mmol, 10 eq.). Yellow solid (129 mg, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (br, 21H,), 7.32 (br, 15H,), 1.28 (s, 36H,), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 151.4, 133.3, 133.1, 132.8, 131.4, 127.8, 127.6, 125.3, 120.2, 88.7, 34.7, 31.1; EI-HRMS: m/z calculated for $M^{\bullet+}$ $C_{84}H_{74}N_4$ 1138.5913 found 1138.5921. FTIR (KBr, cm^{-1}): 2958 (C-H str), 1514 (C=C str), 1105 (C-N str), 828 (C-H ben).

Computational methodologies

The compounds were modelled in Avogadro 1.2.0,[3] and the energy was minimized by the Universal Force Field (UFF) method for generating the initial structural coordinates. A Gaussian (16 version package) software,[4] has been used for density functional theory (DFT) calculations by employing B3LYP (Becke, 3-parameter, Lee–Yang–Parr)[r3] level of theory along with 6-31G* basis set.[5] Geometry optimization was ensured by frequency analysis to make sure that all the atoms were at the local minimum on the molecular potential energy surface (PES). The absence of imaginary frequency supported the accuracy of the optimization results. The contour plots of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) were produced by using the Gauss view 6 program.[6]

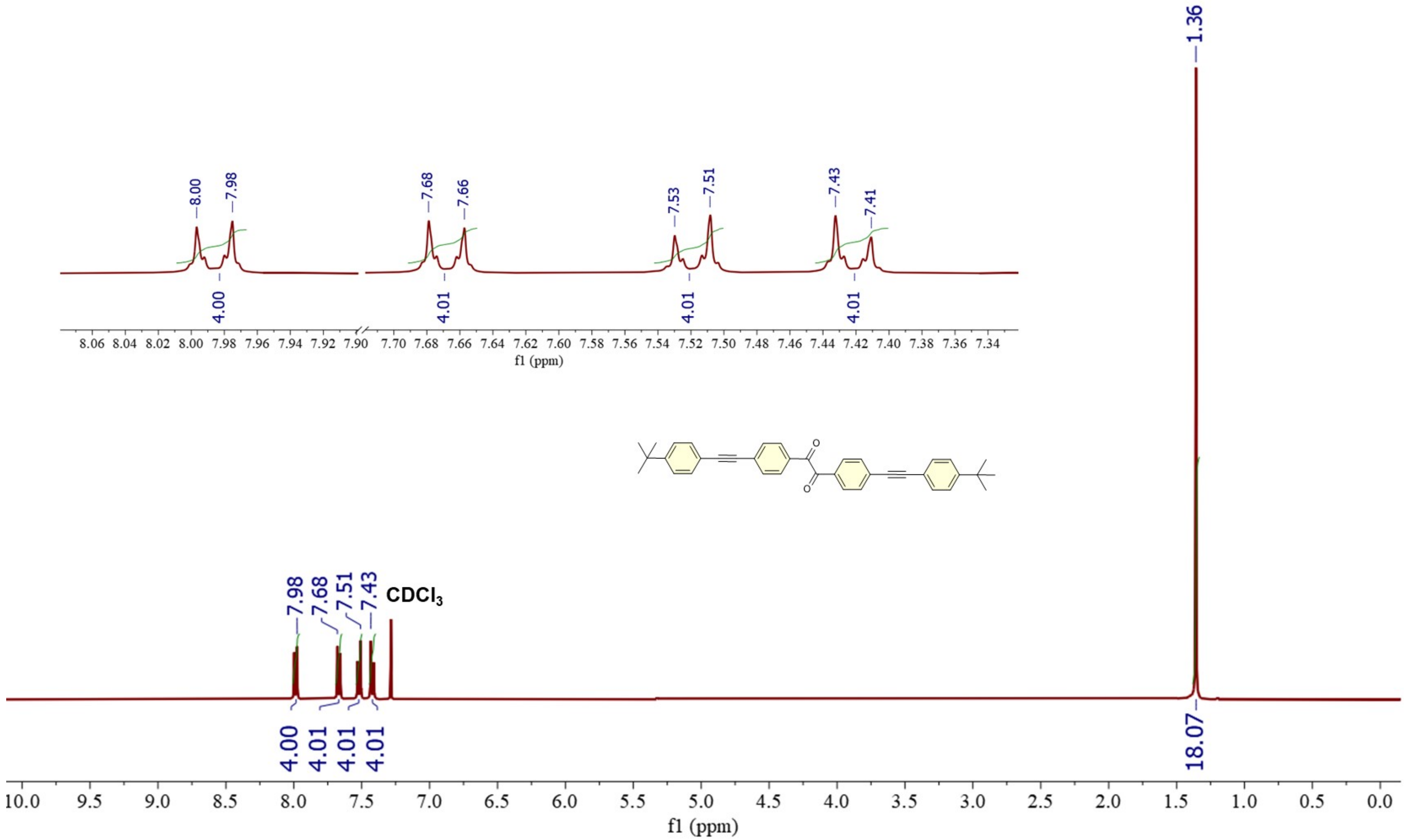


Figure S1: ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz)

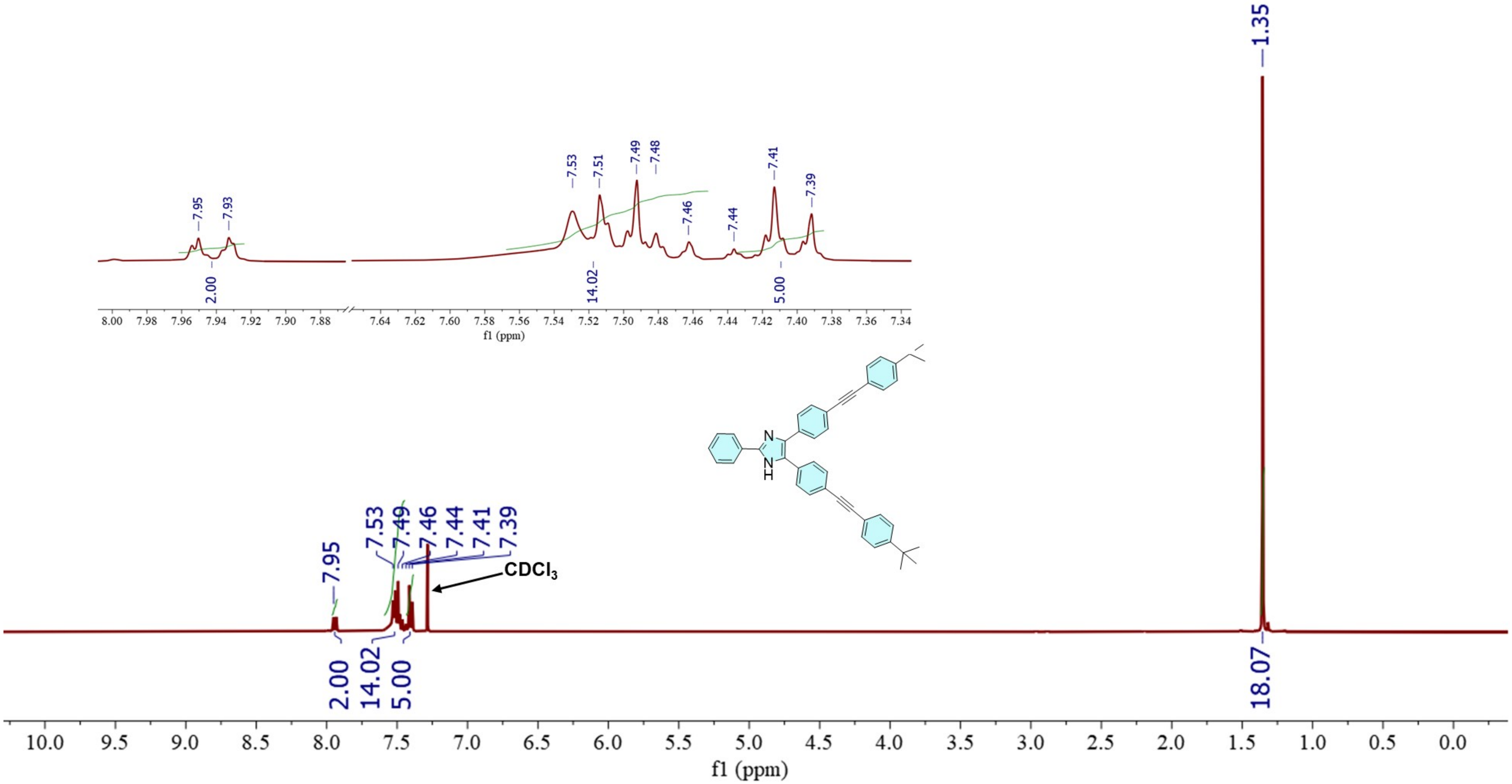


Figure S2: ^{1}H NMR spectrum of **4a** (CDCl$_3$, 400 MHz)

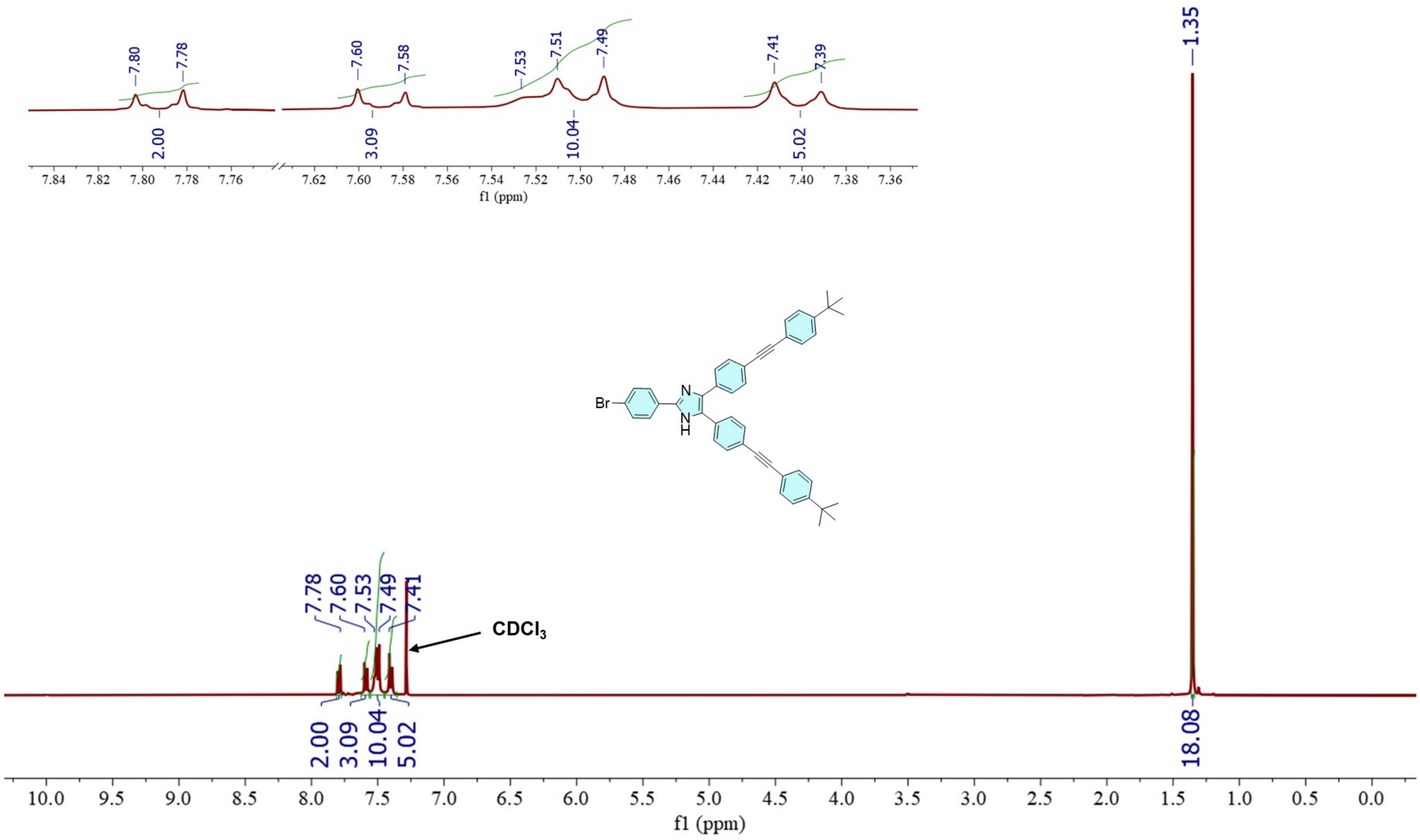


Figure S3: ^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz)

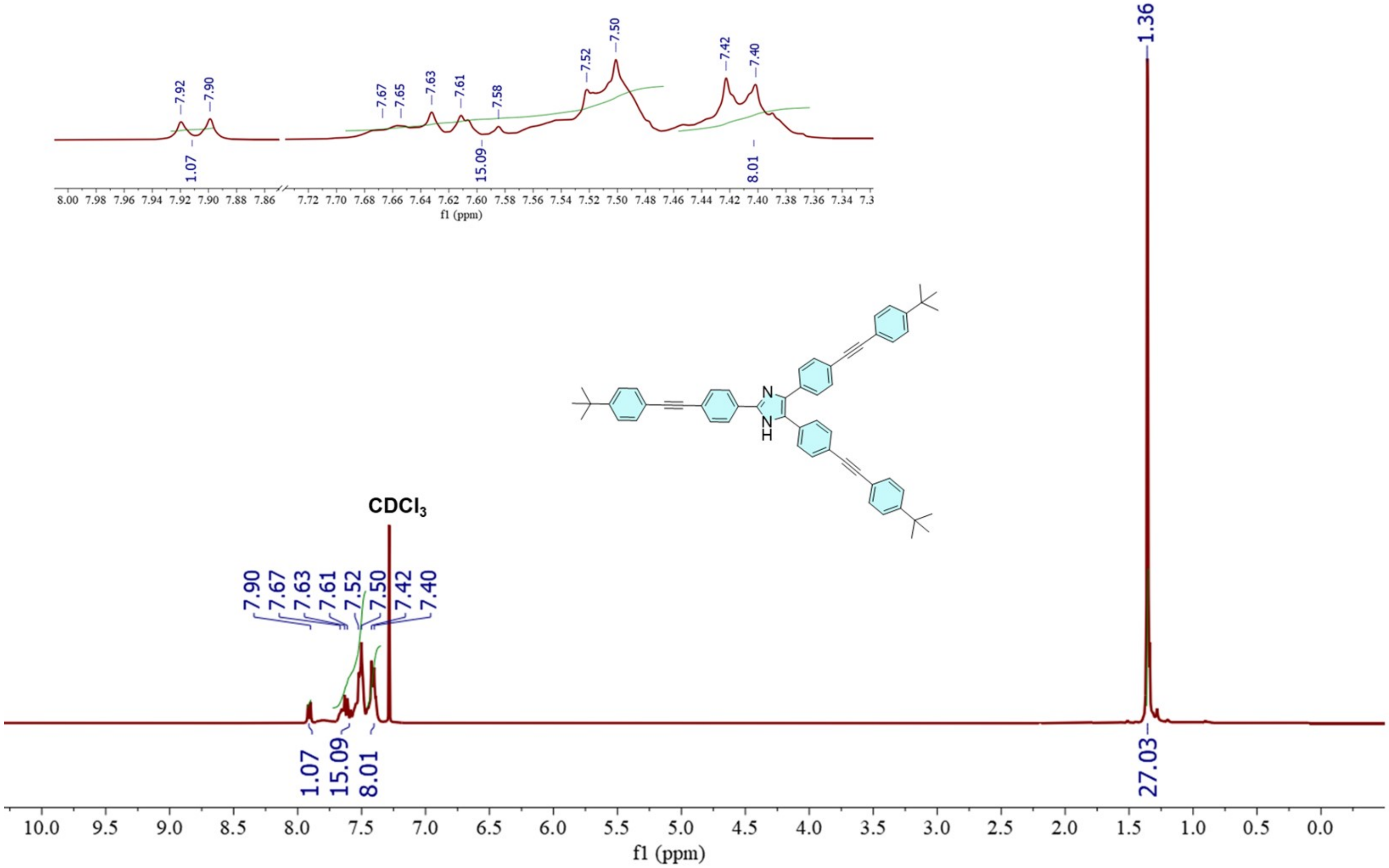


Figure S4: ^{1}H NMR spectrum of **4c** (CDCl$_3$, 400 MHz)

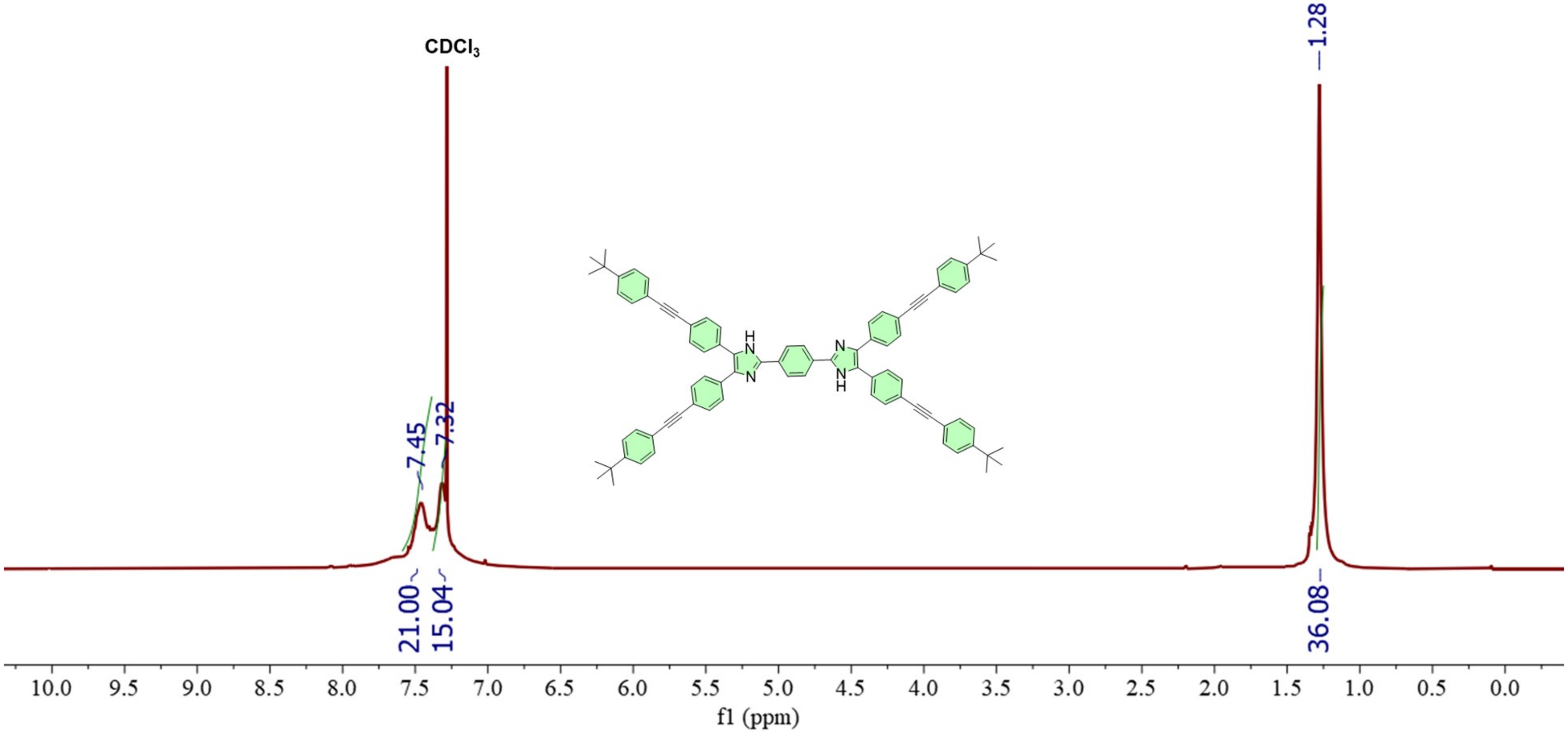


Figure S5: ^{1}H NMR spectrum of **4d** (CDCl$_3$, 400 MHz)

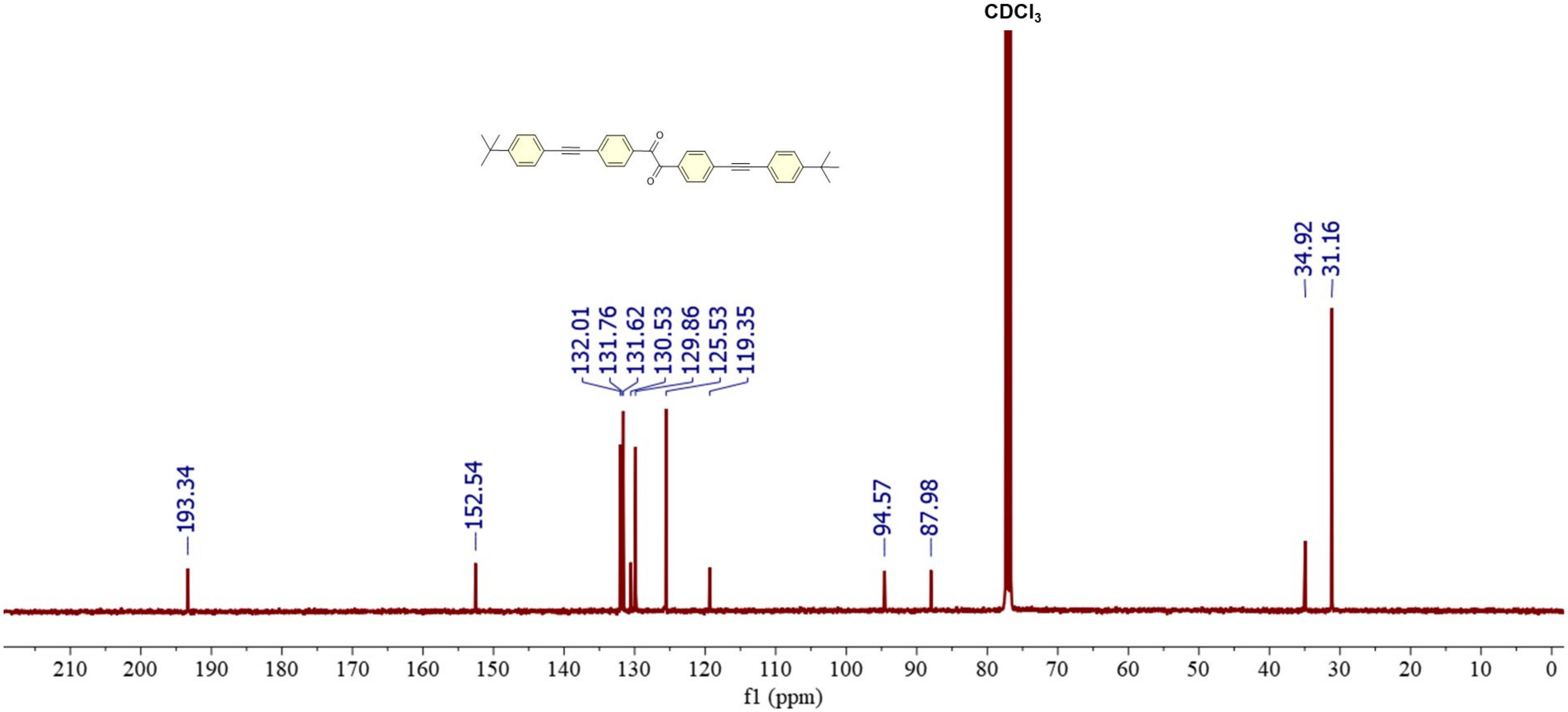


Figure S6: ^{13}C NMR spectrum of **2** (CDCl$_3$, 100 MHz)

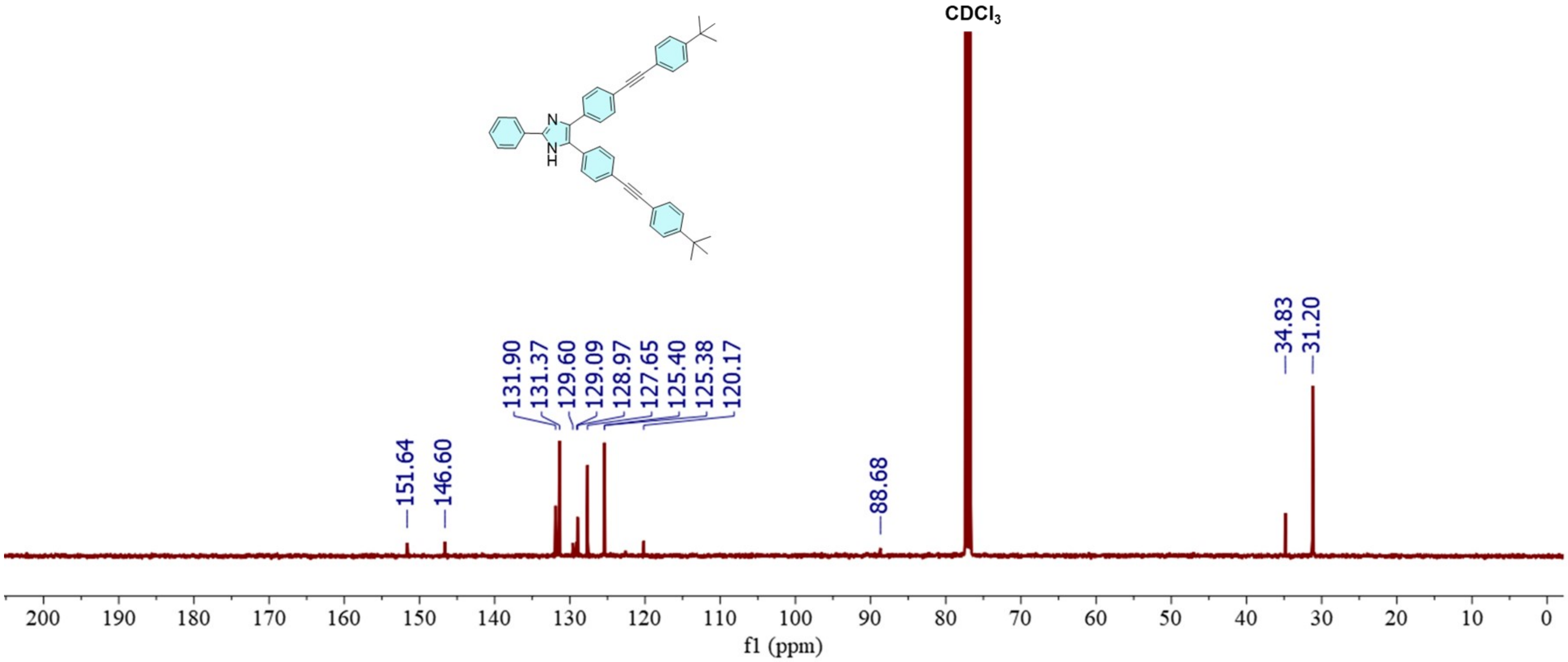


Figure S7: ^{13}C NMR spectrum of **4a** (CDCl$_3$, 100 MHz)

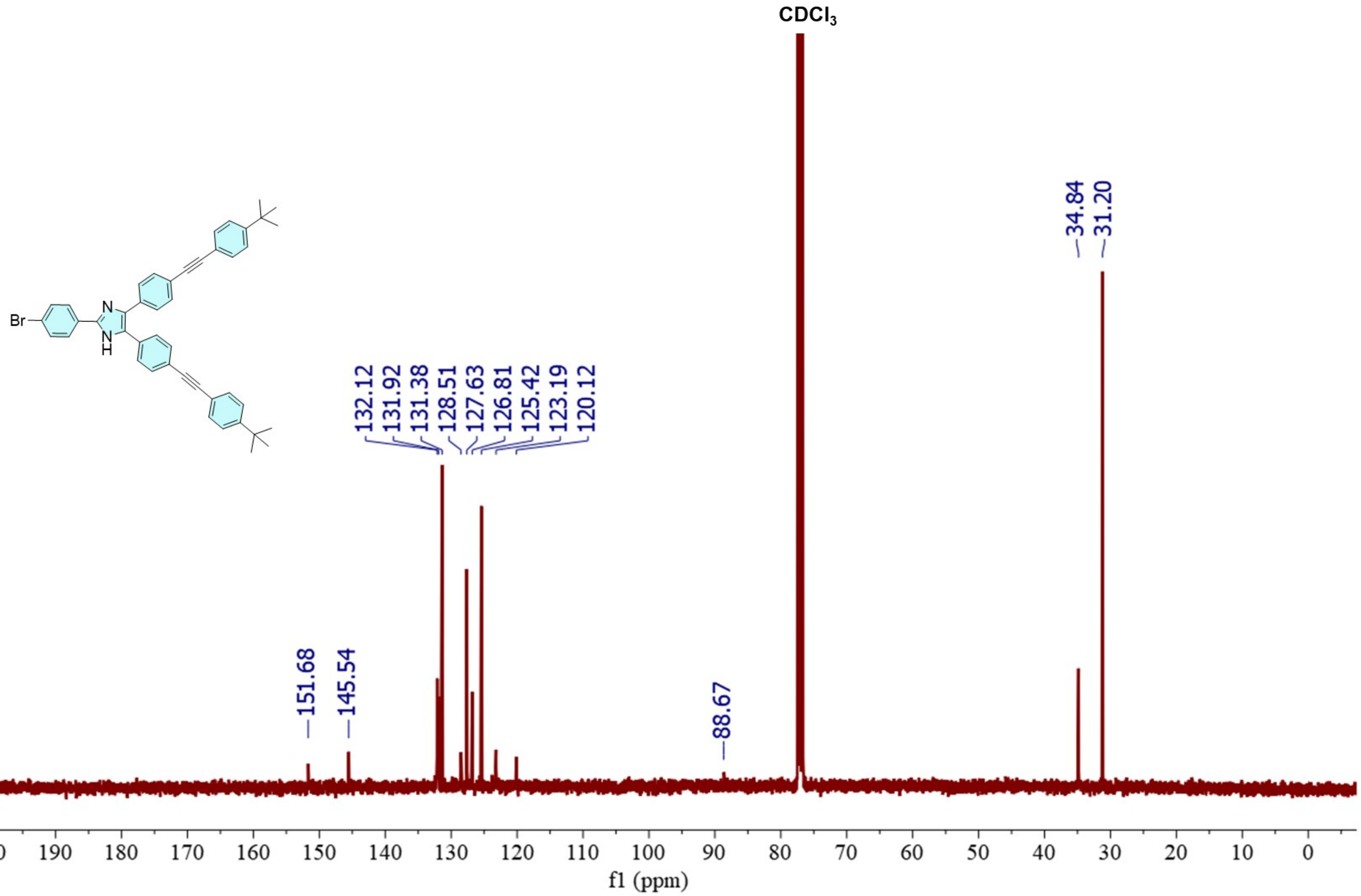


Figure S8: ^{13}C NMR spectrum of **4b** (CDCl$_3$, 100 MHz)

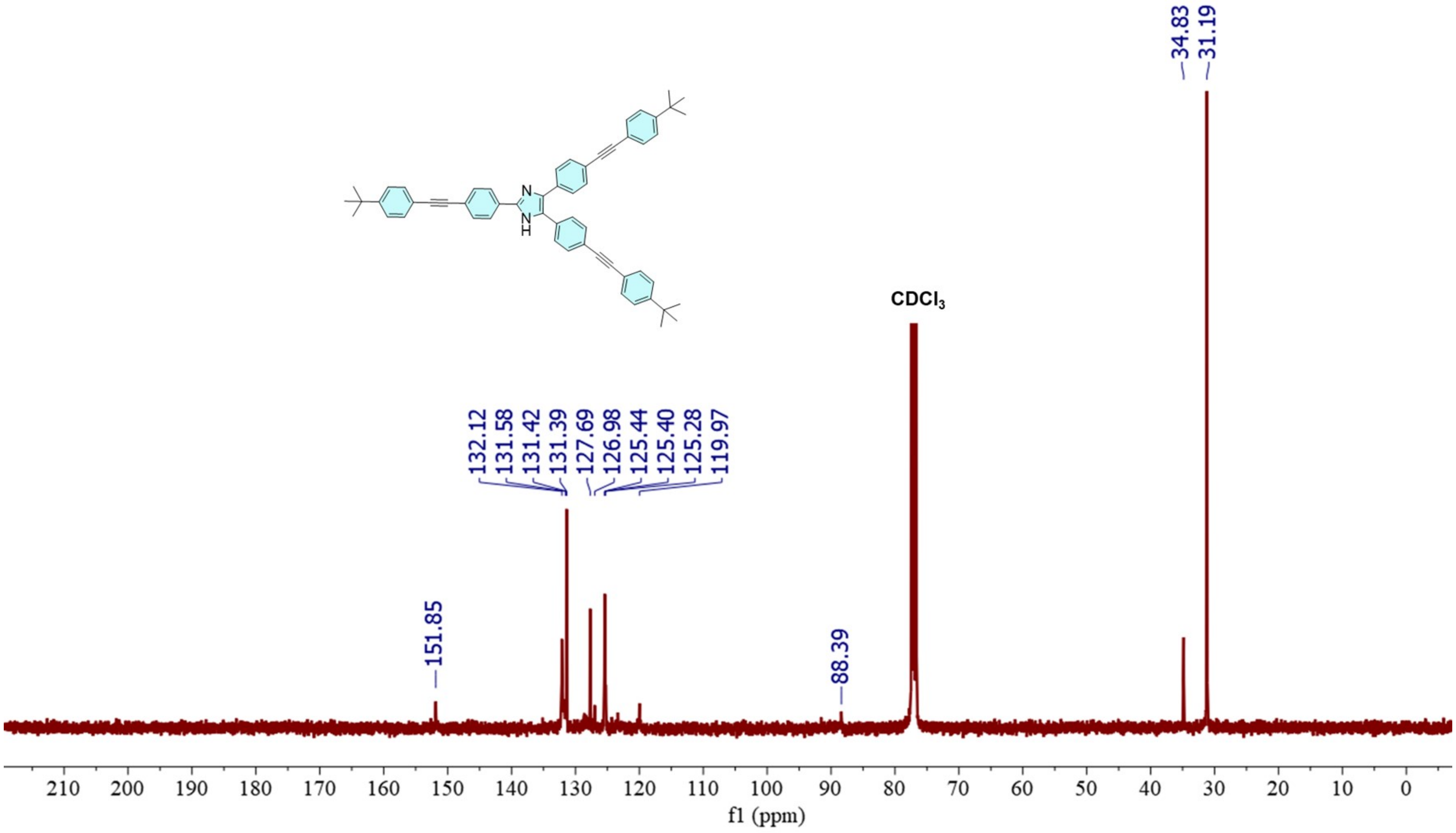


Figure S9: ^{13}C NMR spectrum of **4c** (CDCl$_3$, 100 MHz)

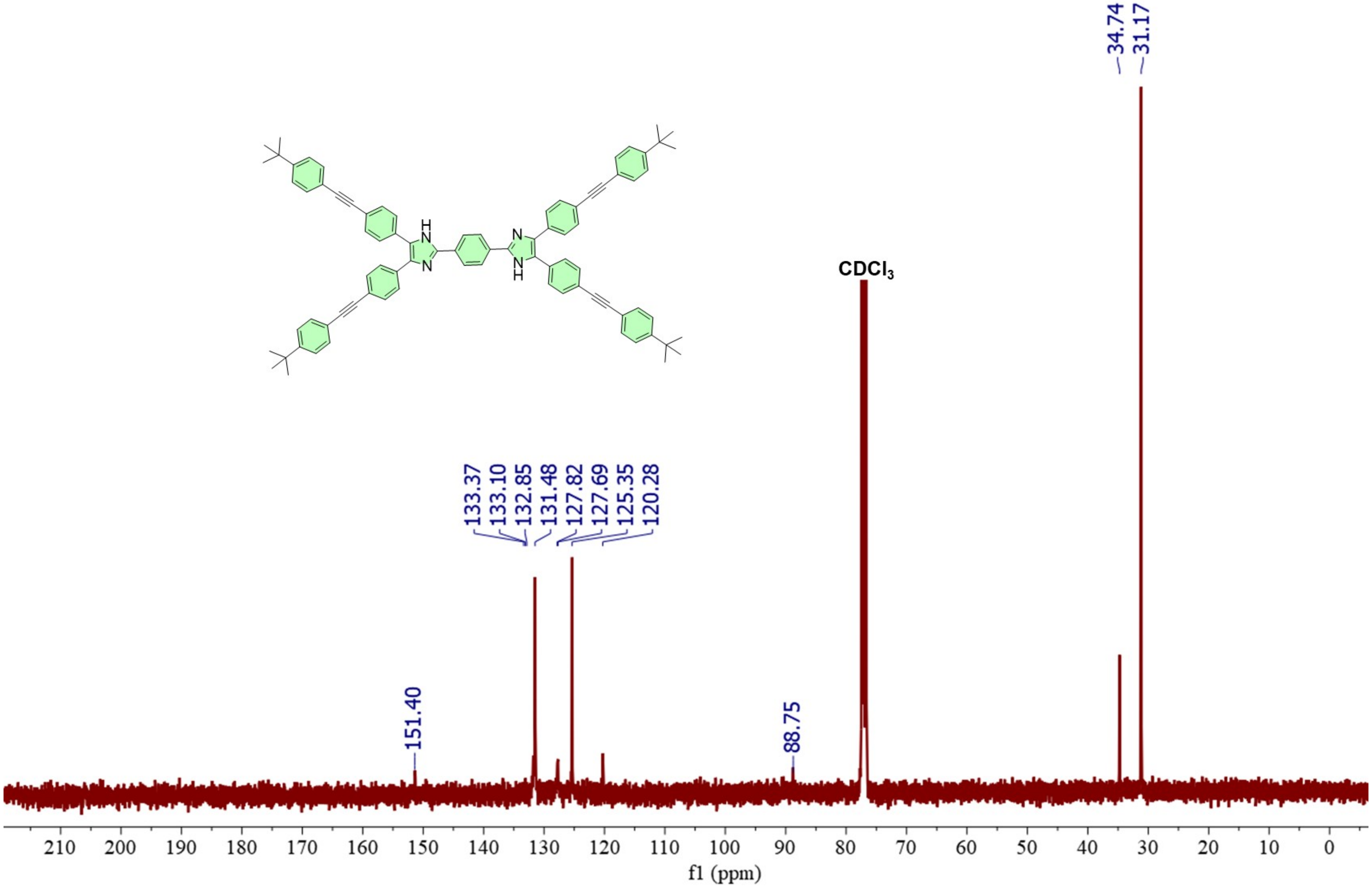


Figure S10: ^{13}C NMR spectrum of **4d** ($CDCl_3$, 100 MHz)

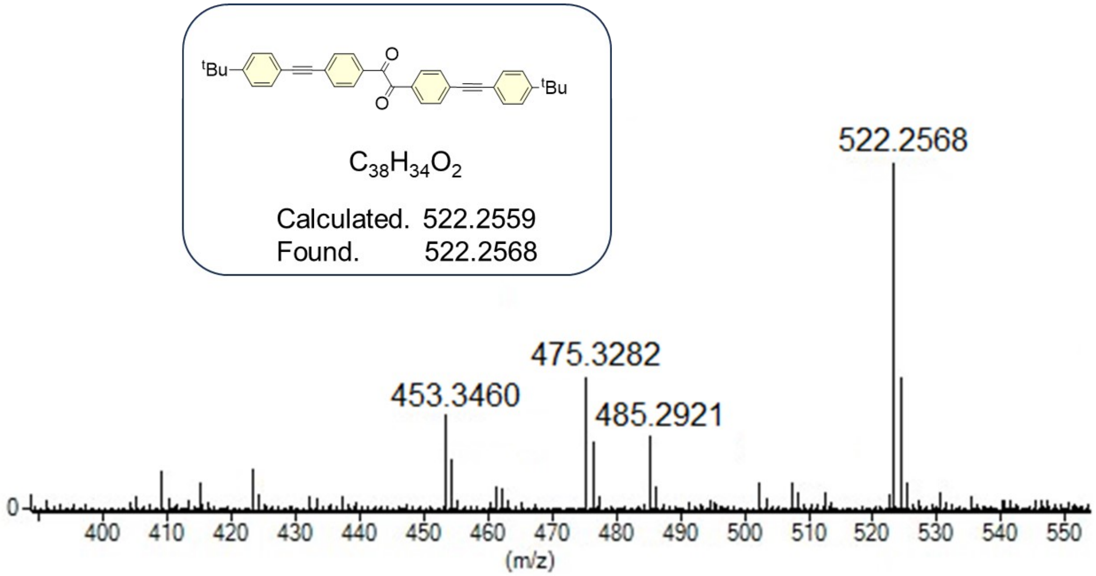


Figure S11: ESI-HRMS spectra of **2**

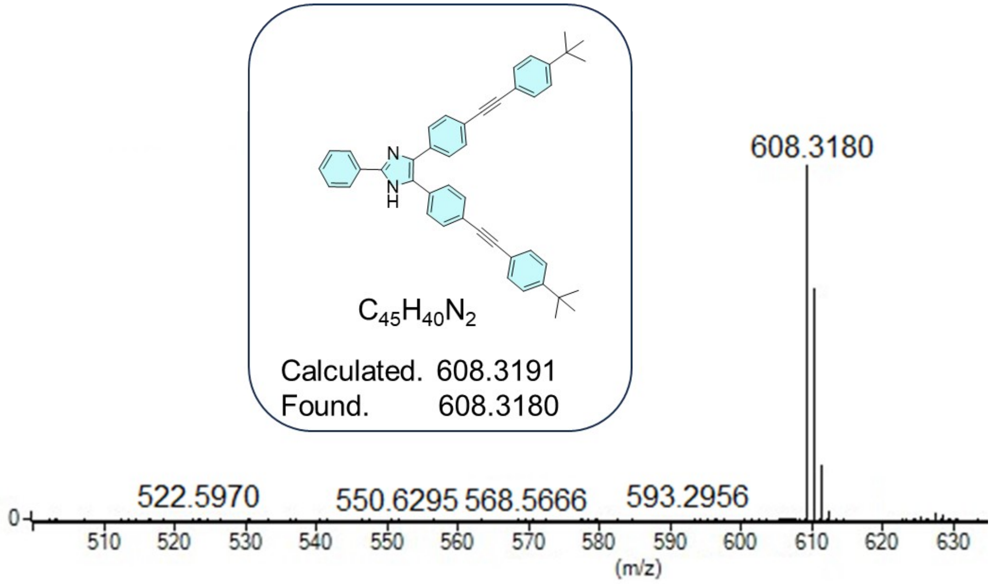


Figure S12: ESI-HRMS spectra of **4a**

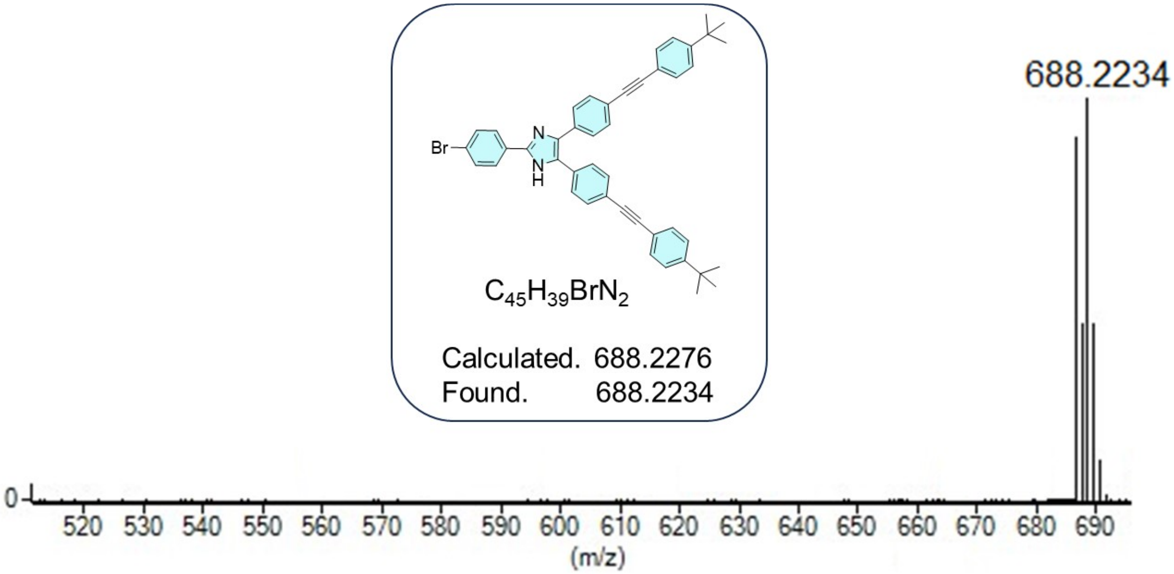


Figure S13: ESI-HRMS spectra of **4b**

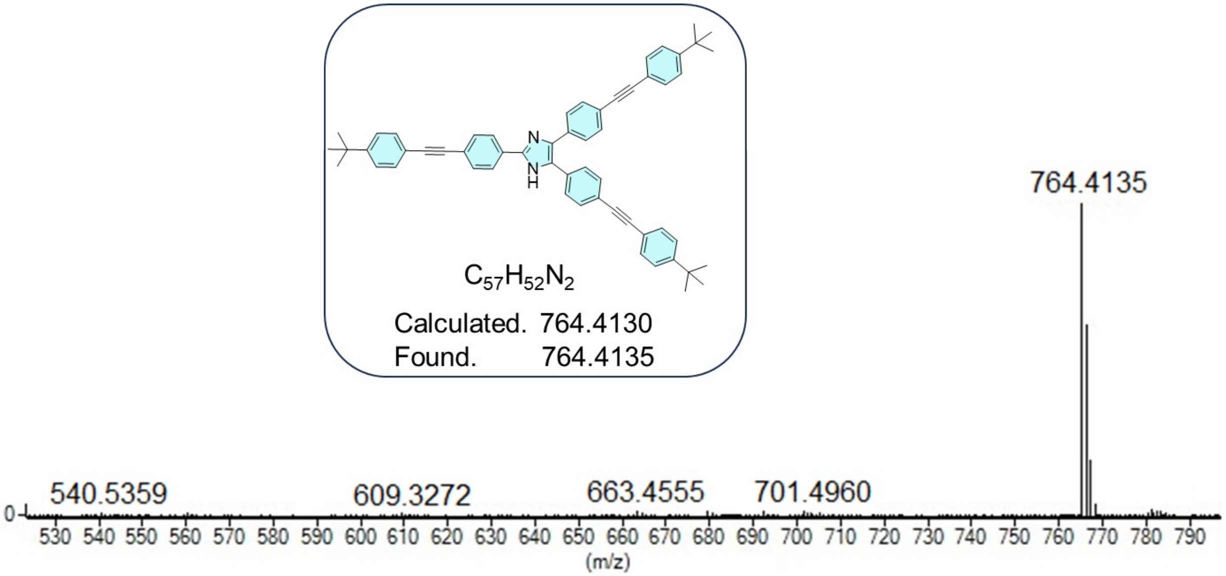


Figure S14: ESI-HRMS spectra of **4c**

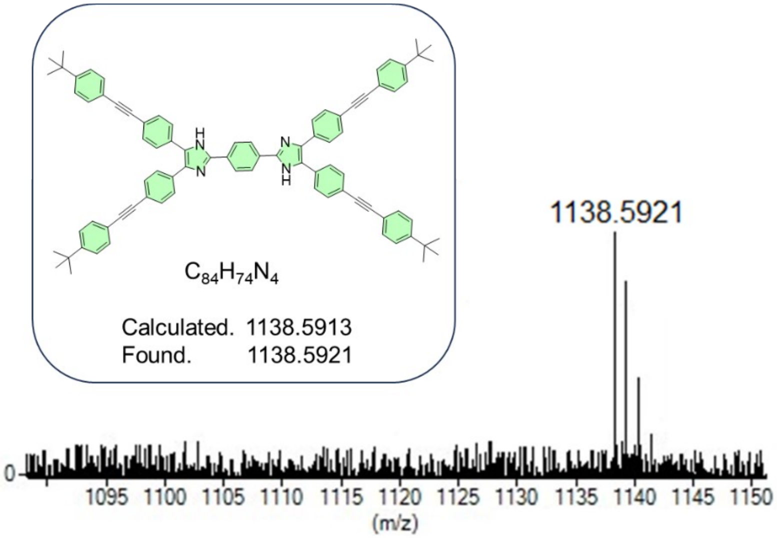


Figure S15: ESI-HRMS spectra of **4d**

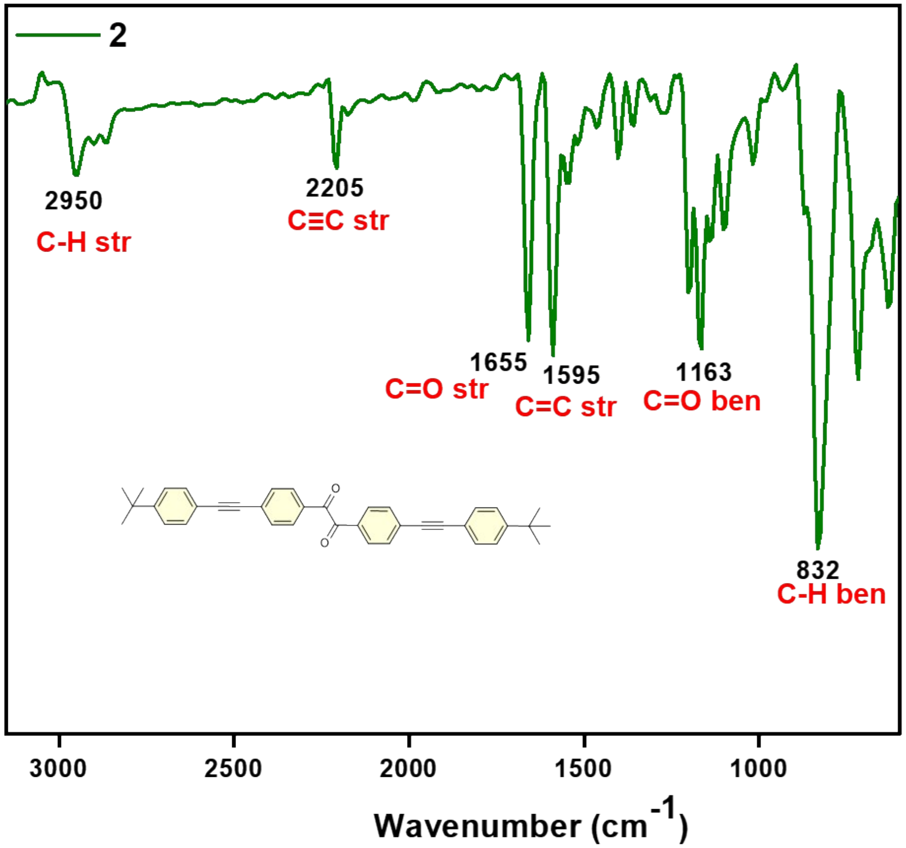


Figure S16: FT-IR spectra of **2**

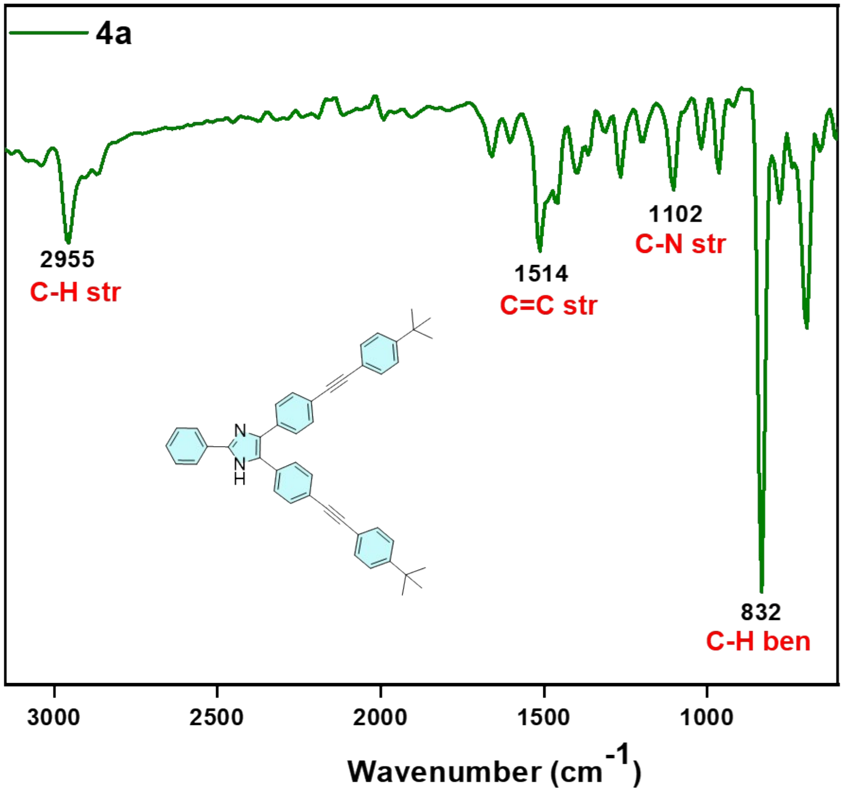


Figure S17: FT-IR spectra of **4a**

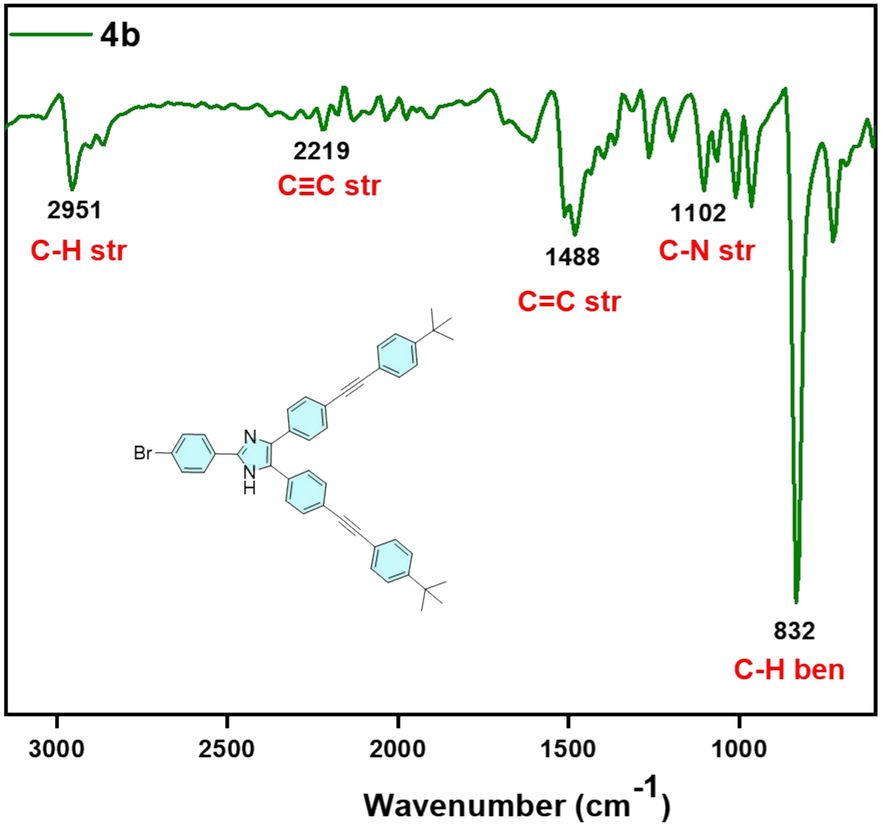


Figure S18: FT-IR spectra of **4b**

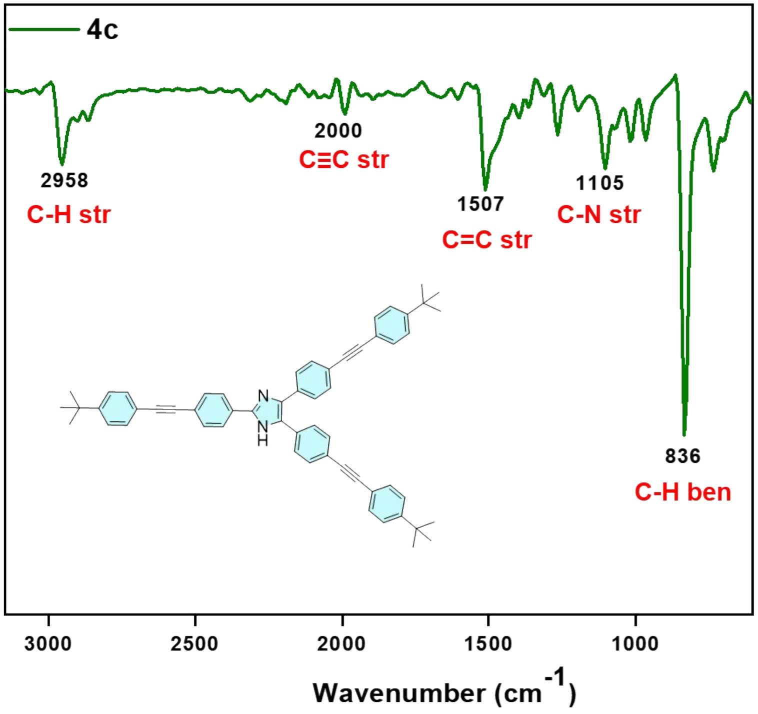


Figure S19: FT-IR spectra of **4c**

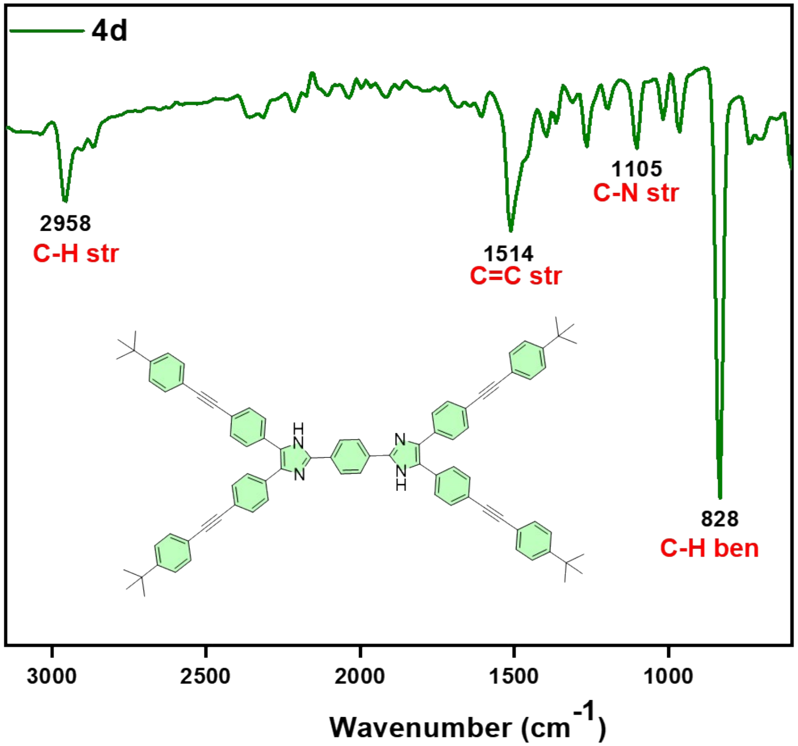


Figure S20: FT-IR spectra of **4d**

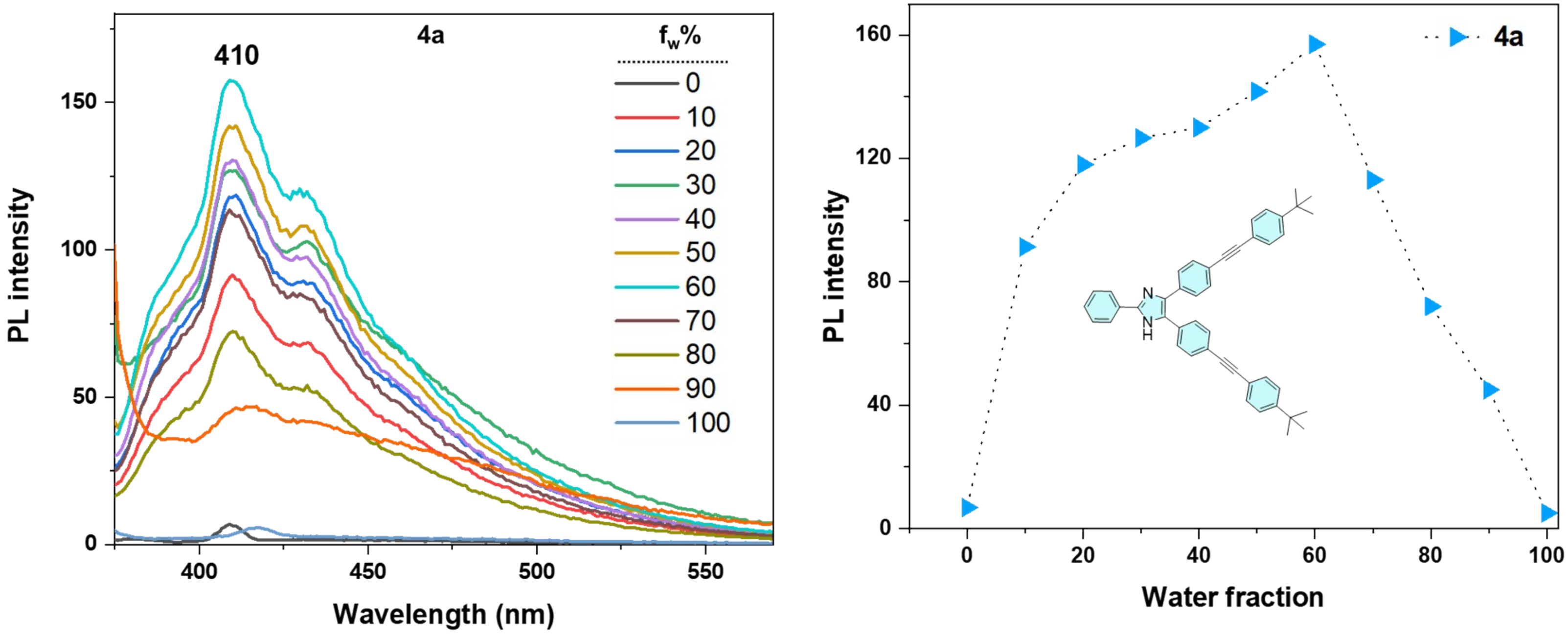


Figure S21: Emission spectra of **4a** in THF/water mixtures (0–100 %) (left); Plot of maximum emission intensity of **4a** versus water fraction (right).

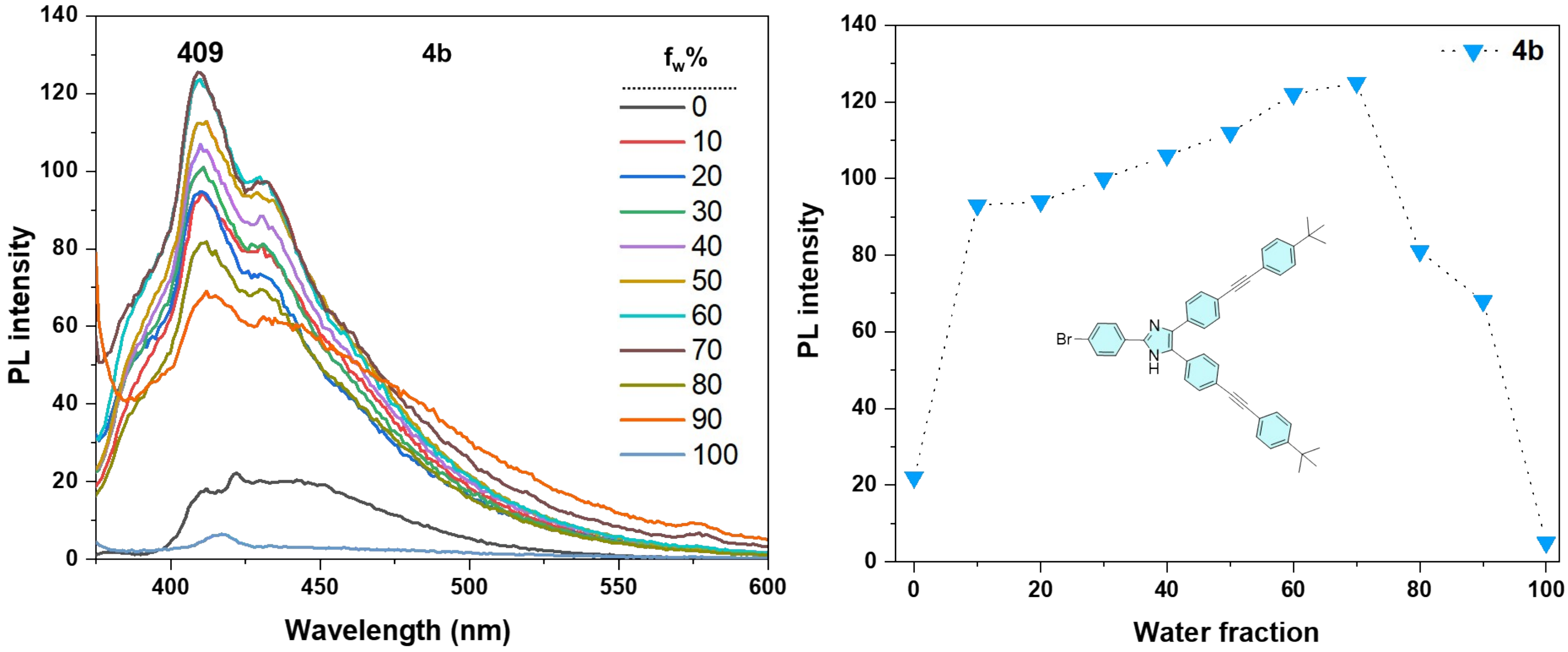


Figure S22: Emission spectra of **4b** in THF/water mixtures (0–100 %) (left); Plot of maximum emission intensity of **4b** versus water fraction (right).

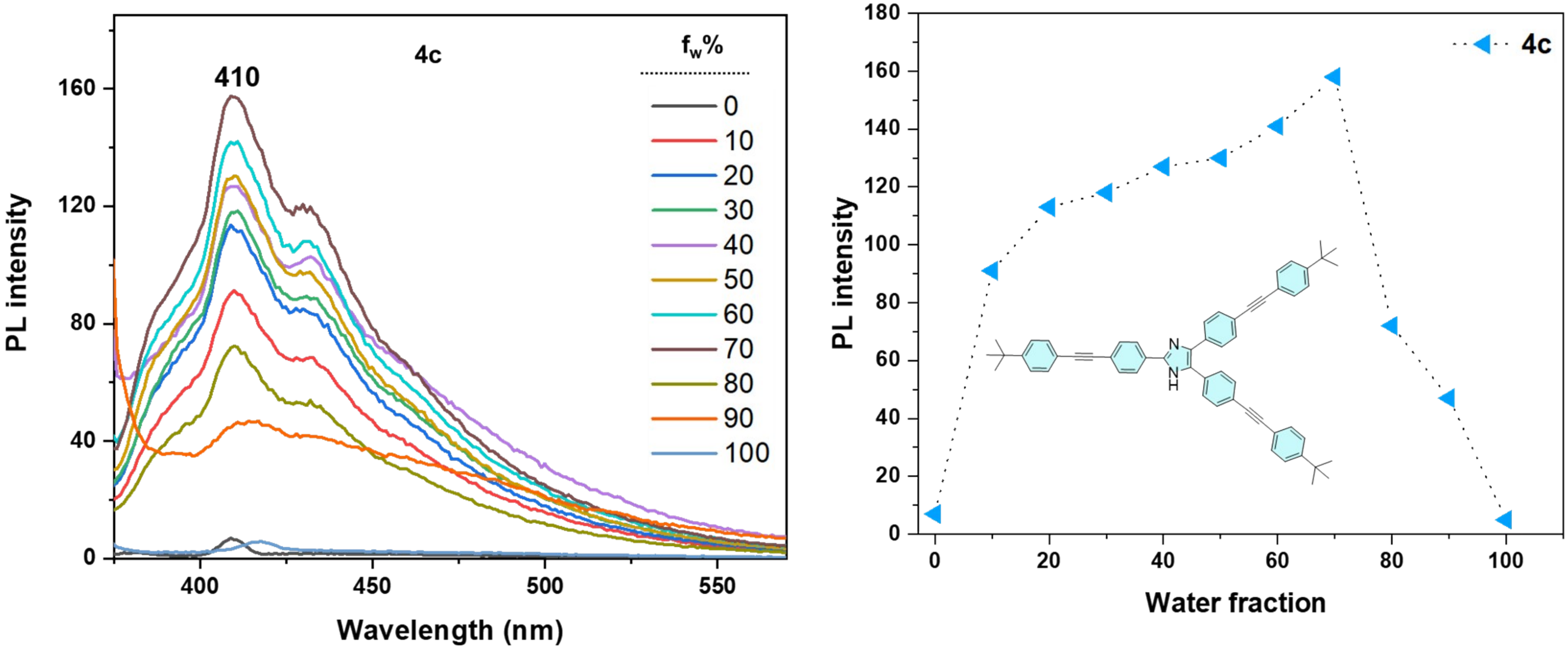


Figure S23: Emission spectra of **4c** in THF/water mixtures (0–100 %) (left); Plot of maximum emission intensity of **4c** versus water fraction (right).

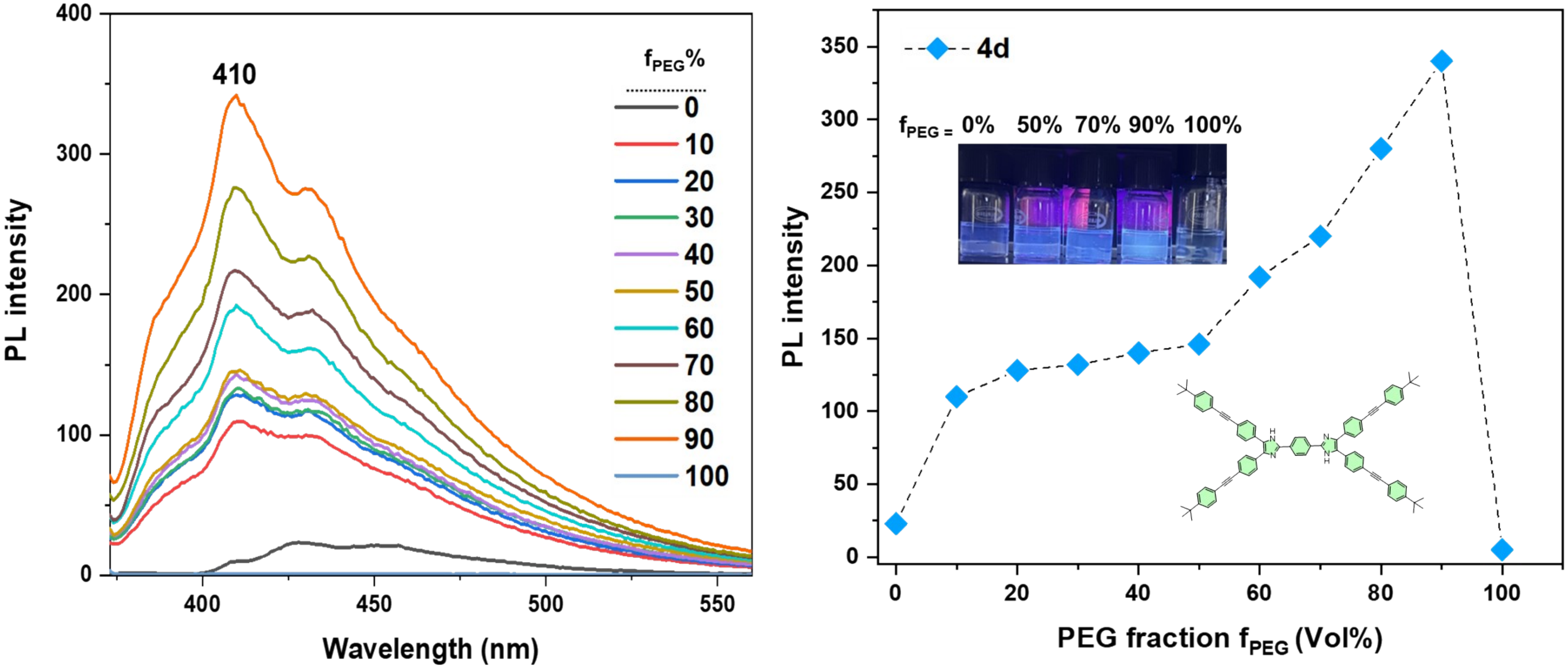


Figure S24: Emission spectra of **4d** in THF/PEG mixtures (0–100 %) (left); Plot of maximum emission intensity of **4d** versus water fraction (right).

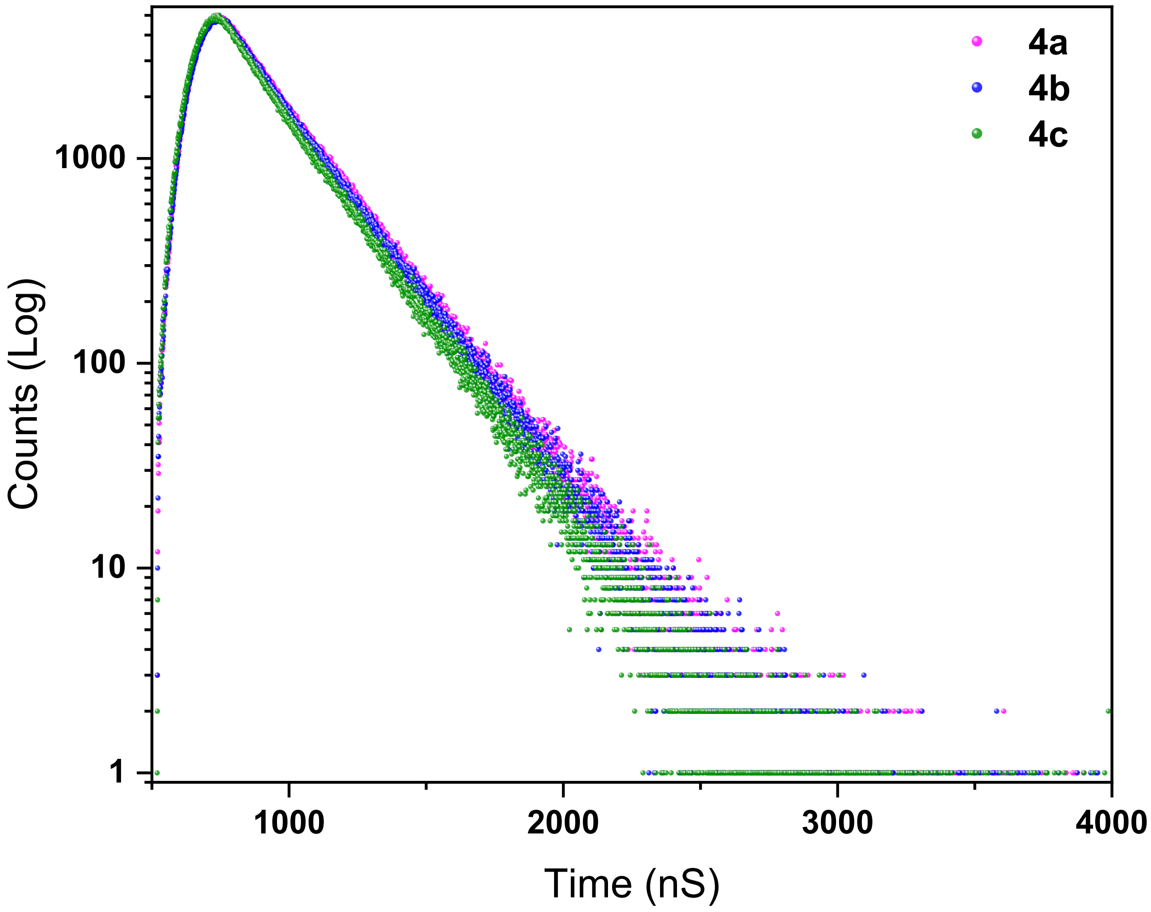


Figure S25: Fluorescence lifetime decay profiles of **4a-c**

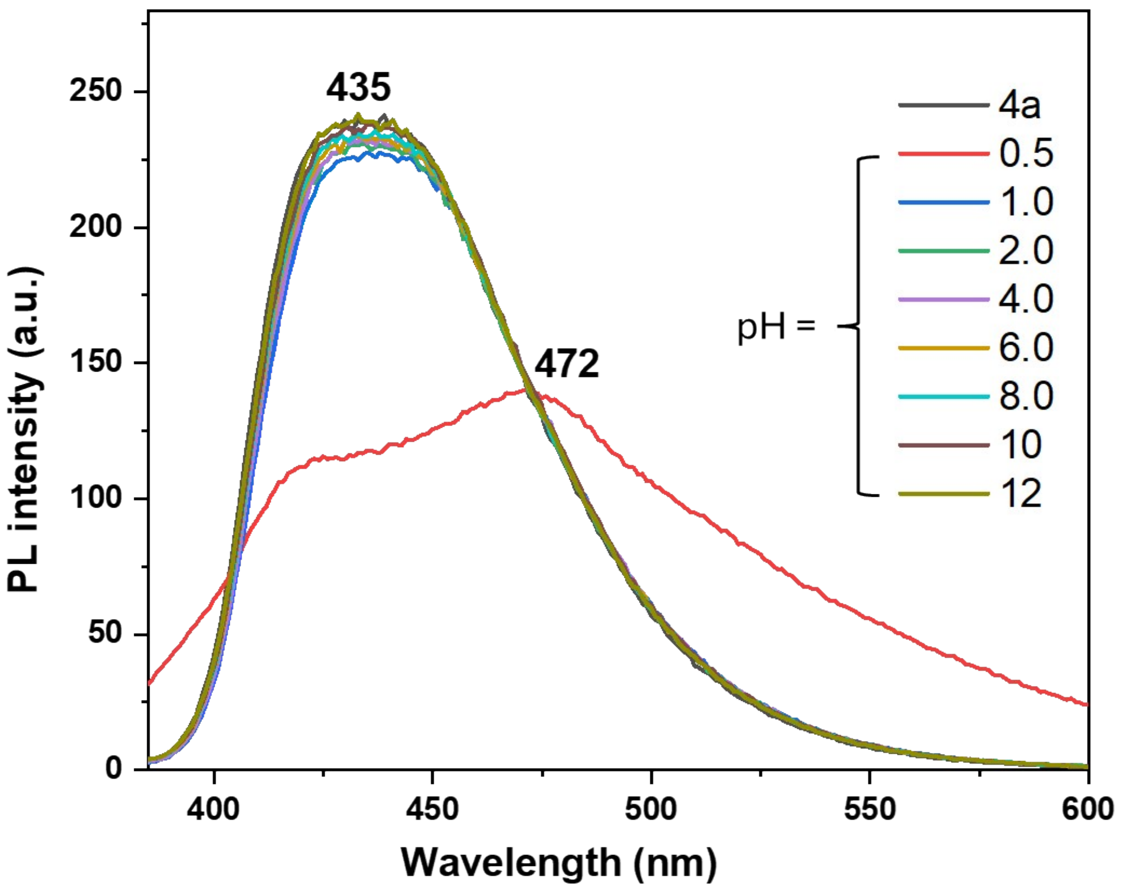


Figure S26: Emission spectra of **4a** (1 x 10^{-7} M in THF, $\lambda_{exc.}$ = 365 nm) in different pH buffer solutions

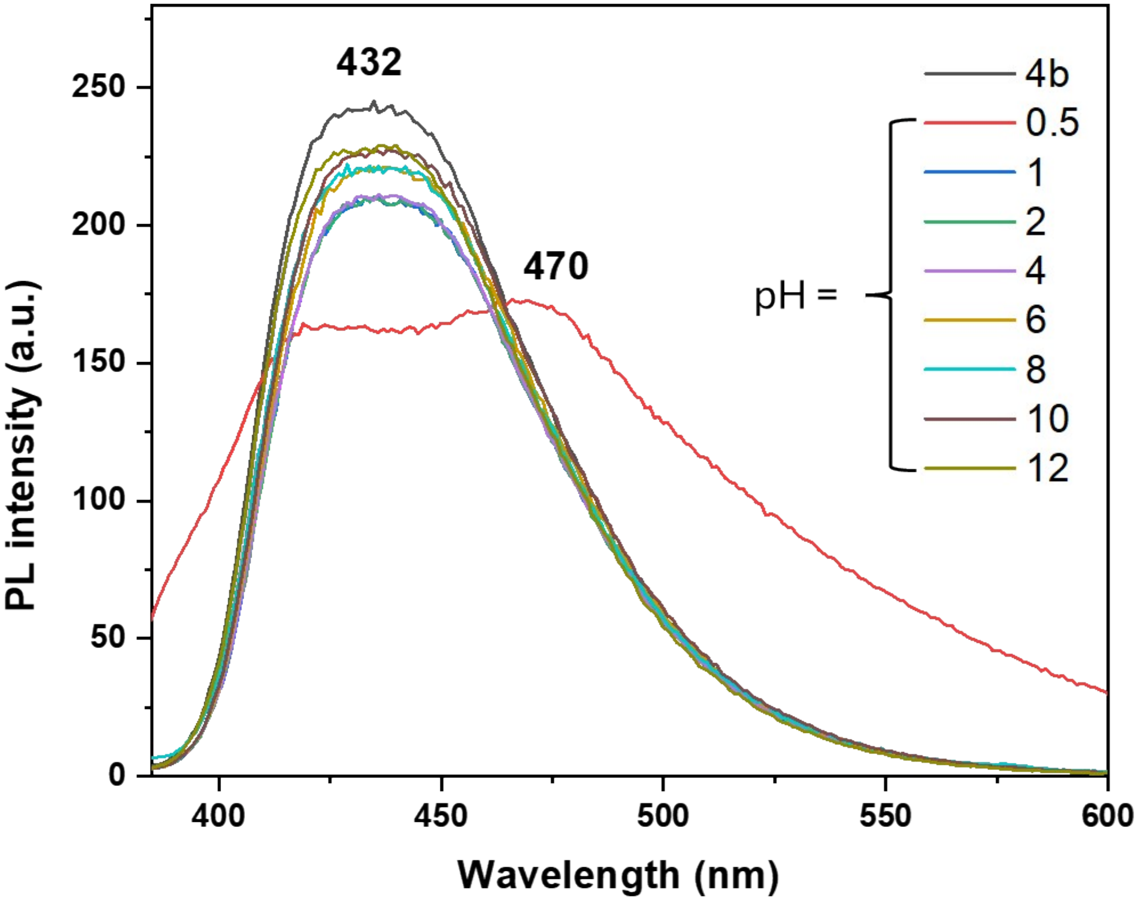


Figure S27: Emission spectra of **4b** (1×10^{-7} M in THF, $\lambda_{exc.}$ = 365 nm) in different pH buffer solutions

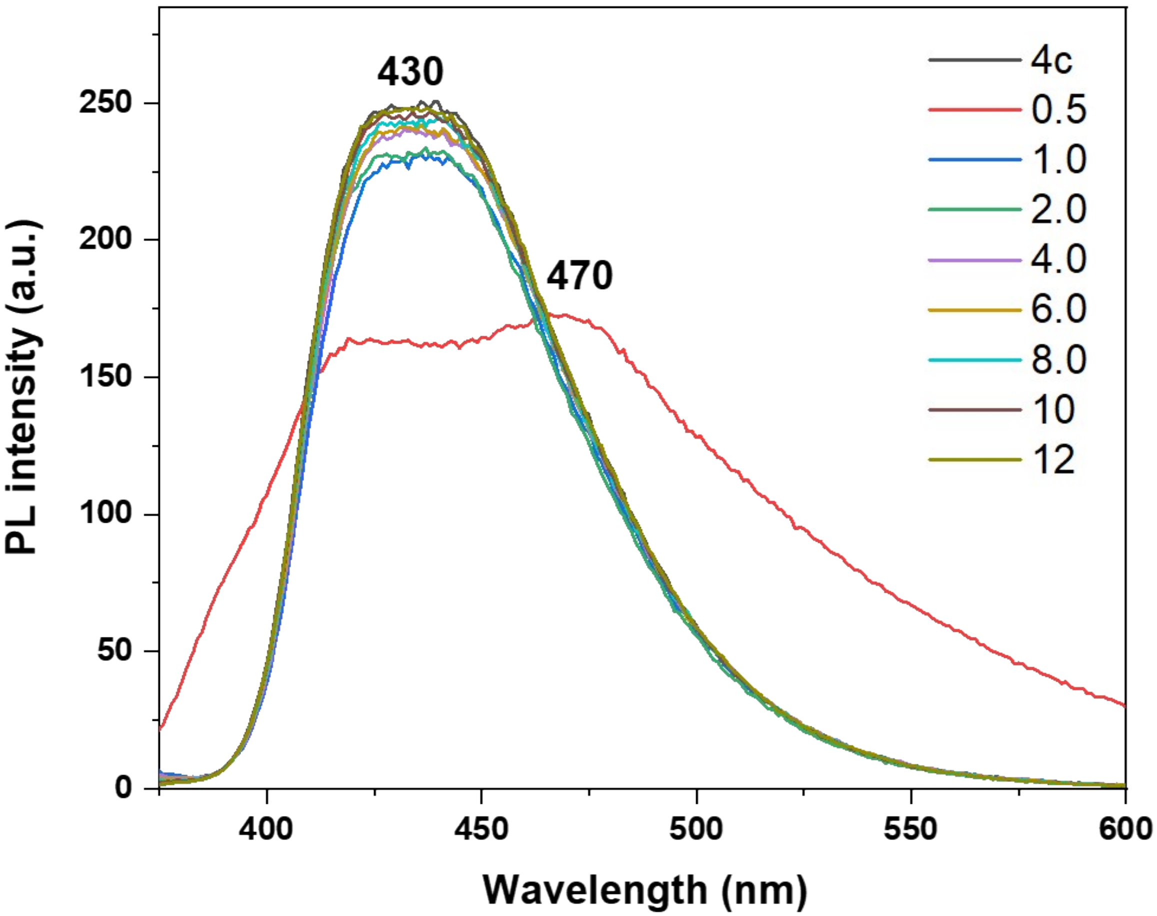


Figure S28: Emission spectra of **4c** (1 x 10^{-7} M in THF, $\lambda_{exc.}$ = 365 nm) in different pH buffer solutions

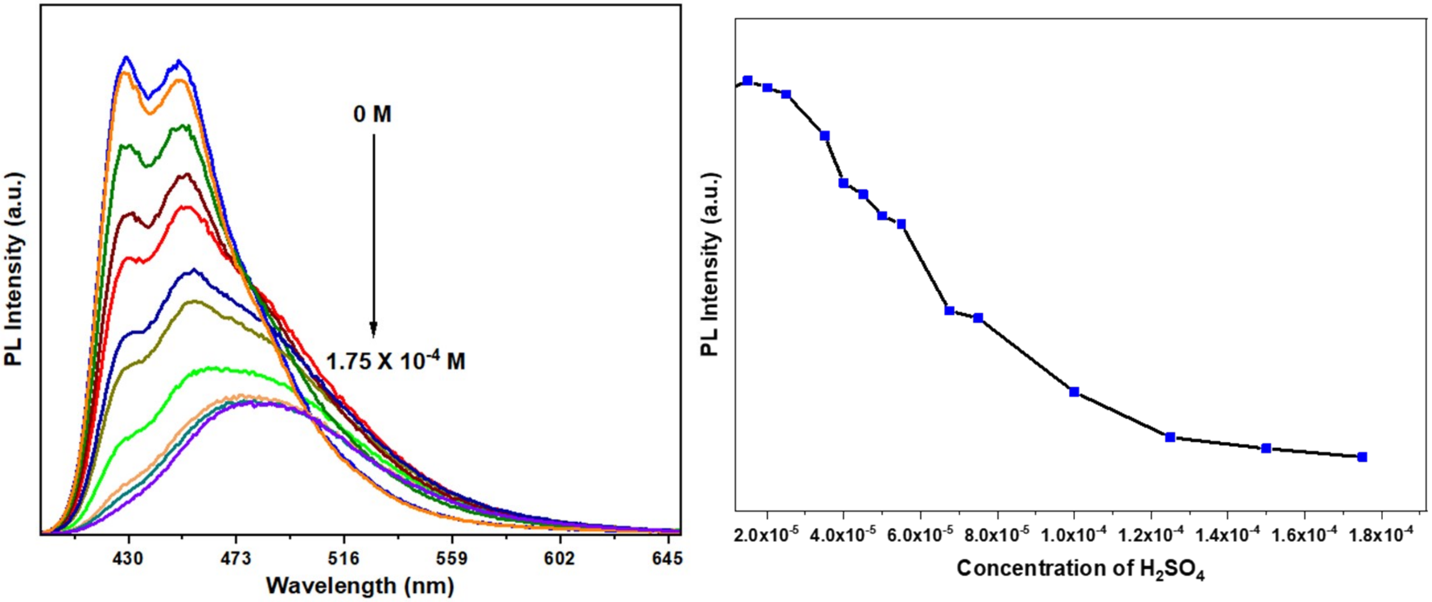


Figure S29: Emission spectra of **4b** (1 x 10^{-6} M in THF, $\lambda_{exc.}$ = 365 nm) in different concentrations of H_2SO_4.

REFERENCES

(1) Baig, N.; Shetty, S.; Abdul Wahed, S.; Hassan, A.; Das, N.; Alameddine, B. Promising CO2 Capture and Effective Iodine Adsorption of Hyper-Cross-Linked Conjugated Porous Organic Polymers Prepared from a Cyclopentannulation Reaction. *ACS Applied Materials & Interfaces* **2024**. DOI: 10.1021/acsami.4c02948.

(2) Baig, N.; Shetty, S.; Wahed, S. A.; Hassan, A.; Das, N.; Alameddine, B. Designing highly porous three-dimensional triazine-bearing covalent organic polymers as prominent adsorbents of carbon dioxide and iodine. *Materials Today Chemistry* **2024**, *41*, 102339. DOI: 10.1016/j.mtchem.2024.102339.

(3) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics* **2012**, *4* (1), 17. DOI: 10.1186/1758-2946-4-17.

(4) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell,

J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian 16, Revision C.01. *Gaussian, Inc., Wallingford CT,* **2016**.

(5) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B* **1988**, *37* (2), 785-789. DOI: 10.1103/PhysRevB.37.785.

(6) GaussView, Version 6.1. *Semichem Inc., Shawnee Mission, KS,* **2016**.