

Supporting Information for
**Three Dimensional Isophlorinoid Tetrapodal Molecular
Cage**

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EXPERIMENTAL METHODS

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by refluxing and distillation over P_2O_5 . Column chromatography was performed by silica open-column gel permeation chromatography with Bio-Beads S-X1 (BIO-RAD). ^1H NMR spectra were recorded on a JEOL 400 MHz and BRUKER 400 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm). Electronic spectra were recorded on a Perkin-Elmer λ -950 ultraviolet–visible (UV–vis) spectro-photometer. High Resolution Mass spectra were obtained using WATERS G2 Synapt Mass Spectrometer. Single-crystal diffraction analysis data were collected at 100K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). In case of disordered solvent molecules, the contributions to the scattering arising from the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package¹. More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre, CCDC **3** = 2061864, **4** = 2061866. Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) measurements were carried out on a BAS electrochemical system using a conventional three-electrode cell in dry CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAF_6) as the supporting electrolyte. Measurements were carried out under an Ar atmosphere. A glassy carbon (working electrode), a platinum wire (counter electrode), and Ag/Ag^+ (reference electrode) were used.

Density Functional Theory (DFT) Calculations

Quantum mechanical calculations were performed with the Gaussian09² (rev-D) program suite using a High Performance Computing Cluster facility of IISER PUNE. All calculations were carried out by Density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d,p) basis set for all the atoms were employed in the calculations. The molecular structures obtained from single crystal analysis were used to obtain the geometry optimized structures. To simulate the steady-state absorption spectra, the time-dependent TD-DFT calculations were employed on the optimized structures. Molecular orbital contributions were determined using GaussSum 2.2.Program package. The global ring centres for the NICS (0) values were designated at the non-weighted mean centres of the macrocycles. The NICS (0) value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries³.

Synthesis and Characterization

Synthesis

A mixture of tetrathienylethene, **2**, (178 mg, 0.5 mmol) and bithiophene diol, **1** (470 mg, 3 mmol) were stirred in 100 mL of dry dichloromethane. The solution was purged with argon for 10 min. and shielded from light. $\text{BF}_3 \cdot \text{OEt}_2$ (60 μL , 0.5 mmol) was added and stirring continued for 2h. Then, DDQ (283 mg, 2.5 mmol) was added and the mixture was stirred for an additional two hours. Finally solution was passed through short pad of basic alumina column. This mixture was concentrated and further purified by silica gel column chromatography using $\text{CH}_2\text{Cl}_2/\text{Hexane}$ as eluent. Finally the products were isolated through size exclusion chromatography.

Characterisation of cage **3**:

MS (MALDI-TOF-TOF): m/z = 2411.1292 (found), 2411.5480 (calcd. For $\text{C}_{148}\text{H}_{120}\text{S}_{16}$).

UV-Vis (CHCl_3): λ_{max} (ϵ) $\text{L mol}^{-1} \text{cm}^{-1}$ = 532 nm (253000)

NMR Data: $^1\text{H NMR}$ (400 MHz, THF-d_8 , 198 K) δ 7.34 (m, 8H), 7.06 (s, 4H), 6.94 (m, 12H), 6.82 (s, 8H), 6.22 (m, 12H), 6.04 (d, $J=10.4$ Hz, 4H), 2.28 (m, 36H), 2.04 (s, 12H), 1.91 (d, $J=16.8$ Hz, 24H).

Crystal data: $\text{C}_{148} \text{H}_{120} \text{S}_{16}$, (+ Solvent) (M_r 2411.40), tetragonal, space group $P -4 n 2$, $a = 26.025(8)$, $b = 26.025(8)$, $c = 12.283(5)$ \AA , $\alpha=90$, $\beta=90$, $\gamma=90$.
 $V = 8319.28(6)$ \AA^3 , $Z = 2$, $T = 100(2)$ K, $D_{\text{calcd}} = 0.963 \text{ cm}^{-3}$, $R_1 = 0.095$ (5517), R_w (all data) = 0.2857(7428), GOF = 1.038.

Characterisation of macrocycle **4**:

HR-MS (ESI-TOF): m/z = 1560.2346 (found), 1560.2283 (calcd. For $\text{C}_{92}\text{H}_{72}\text{S}_{12}$).

UV-Vis (CHCl_3): λ_{max} nm (ϵ) $\text{L mol}^{-1} \text{cm}^{-1}$ = 443 (95240), 470 (89900), 575 (80000).

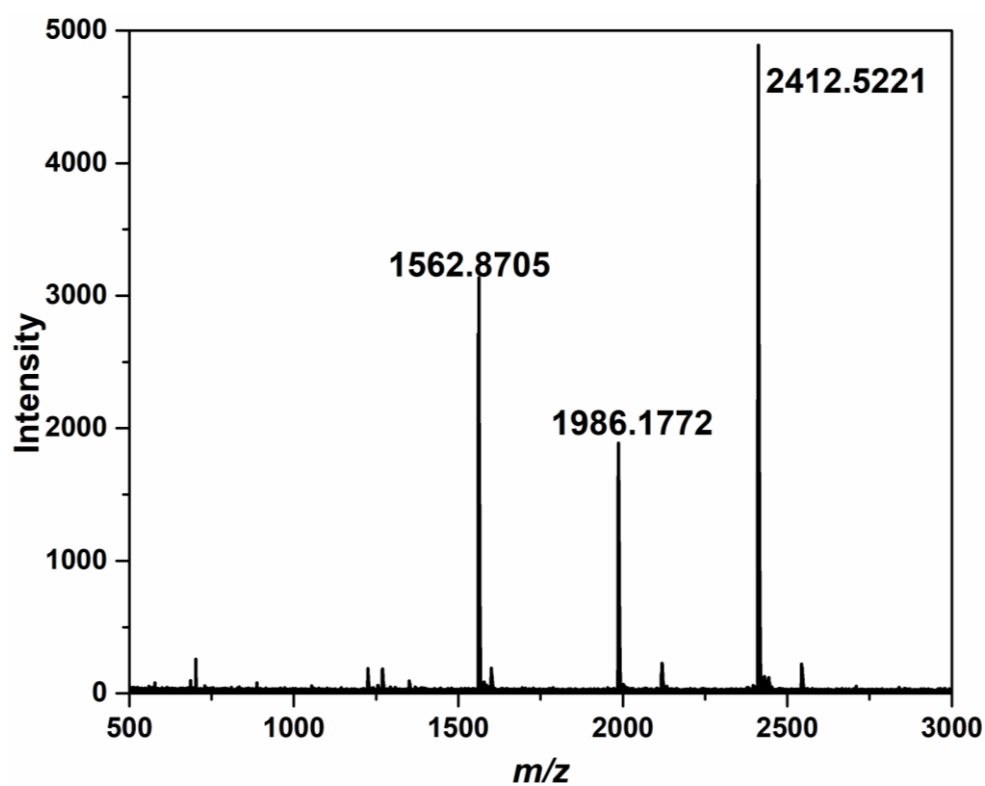
NMR Data: $^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , 223 K) δ 7.39 (m, 4H), 7.21 (m, 4H), 7.11 (m, 8H), 7.01 (m, 4H), 6.9 (m, 8H), 6.75 (d, $J = 6$ Hz, 2H), 6.35 (d, $J = 4$ Hz, 2H), 6.25 (m, 4H), 2.27 (d, $J = 15.2$ Hz, 12H), 2.01 (s, 24H).

Crystal data: $\text{C}_{92} \text{H}_{72} \text{S}_{12}$, (M_r 1562.12), monoclinic, space group $P 2_1/c$, $a = 13.11(3)$, $b = 25.03(6)$, $c = 28.95(7)$ \AA , $\alpha = 90$, $\beta = 90.27(3)$, $\gamma = 90$.
 $V = 9495(40)$ \AA^3 , $Z = 4$, $T = 100(2)$ K, $D_{\text{calcd}} = 1.093 \text{ cm}^{-3}$, $R_1 = 0.1378$ (9215), R_w (all data) = 0.3744(16829), GOF = 1.053.

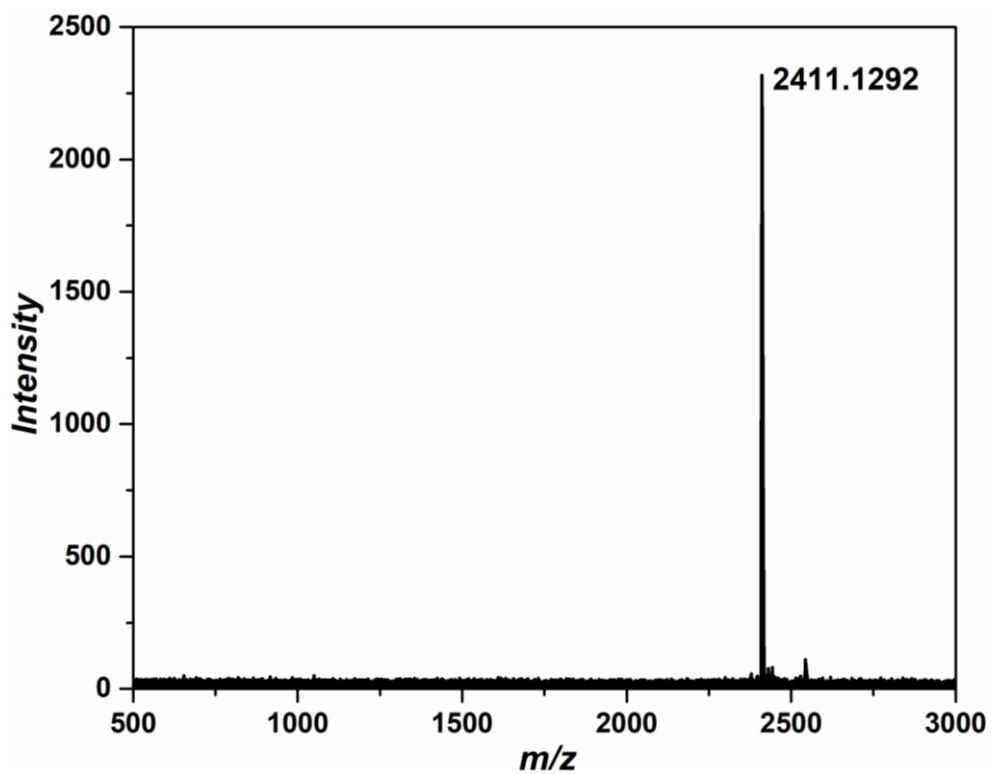
Characterisation of macrocycle **6**:

HR-MS (ESI-TOF): $m/z = 1395.8707$ (found), 2791.7397 (calcd. For $C_{124}H_{32}F_{40}S_{16}$).

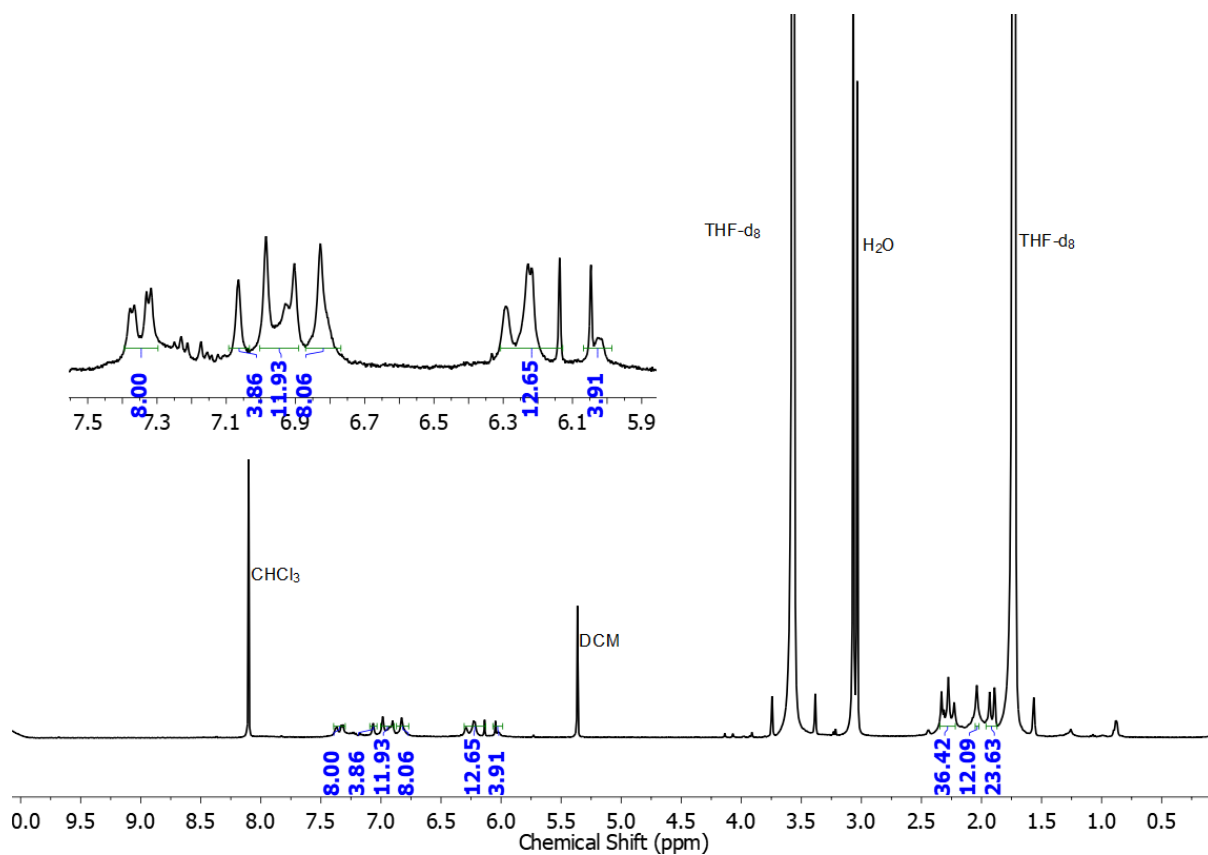
NMR Data: 1H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.96 (m, 16H), 6.78 (d, $J = 8$ Hz, 8H), 6.27 (d, $J = 8$ Hz, 8H).



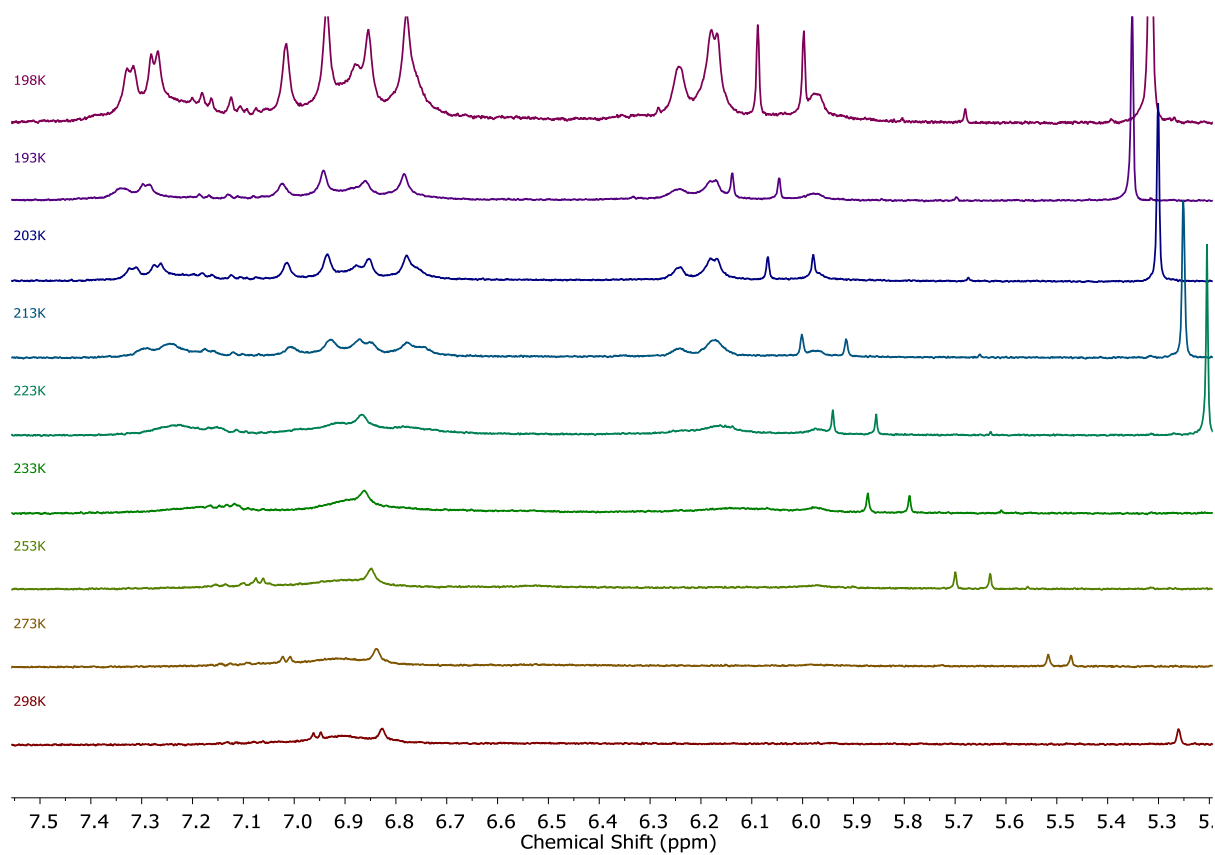
S1: MALDI-TOF/TOF mass spectrum of the reaction mixture corresponding to **3**, **4** and **5**



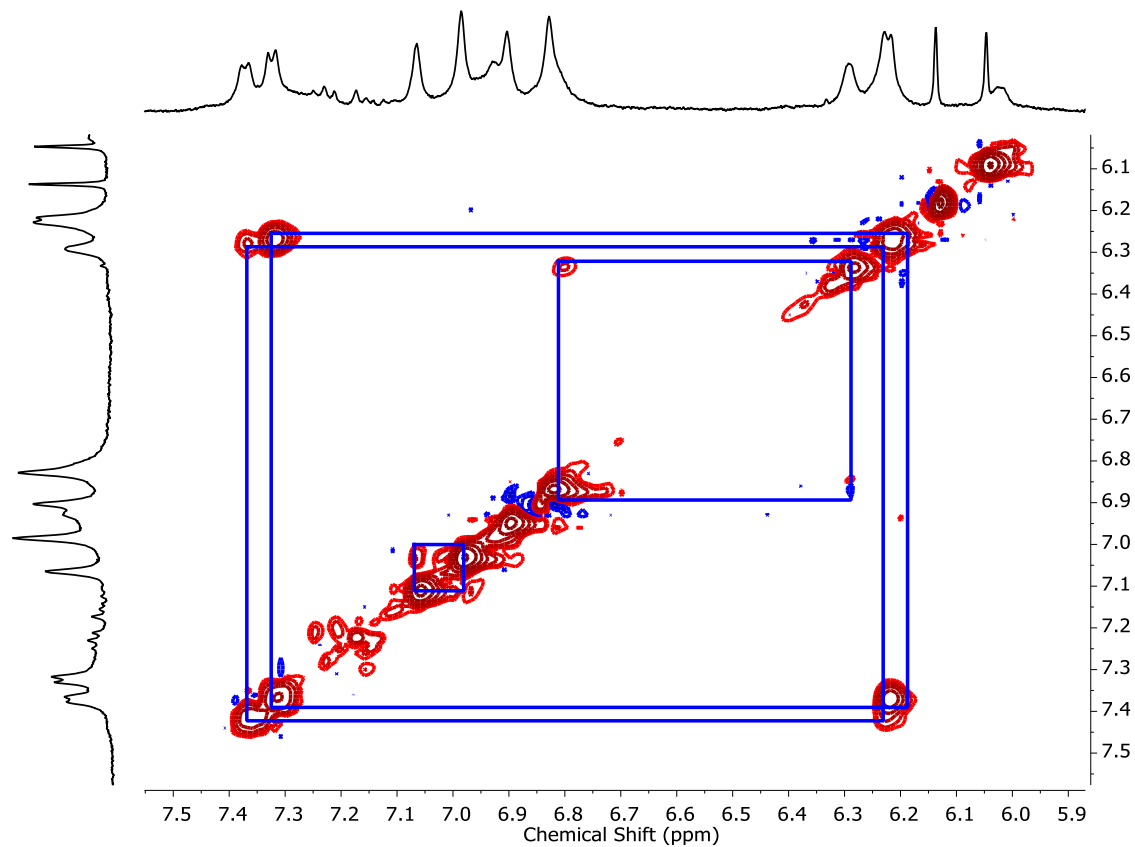
S2: MALDI-TOF/TOF mass spectrum of **3**.



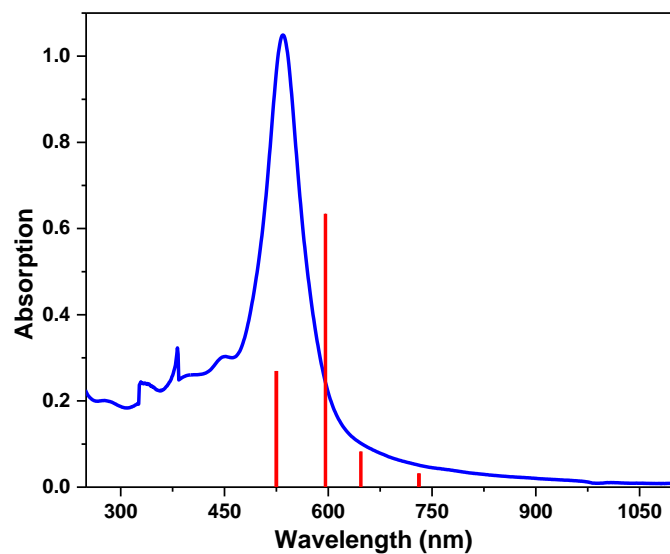
S3: ¹H NMR spectrum of **3** in THF- d_8 at 198 K



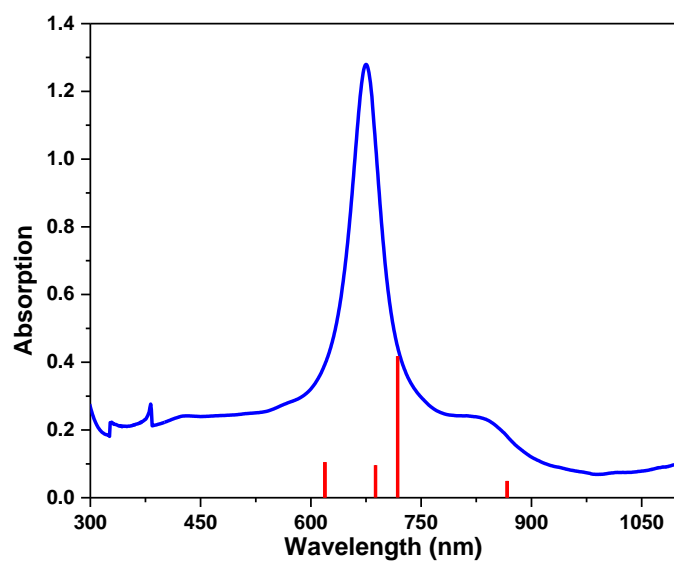
S4: Variable temperature ^1H NMR spectrum of **3** in $\text{THF-}d_8$



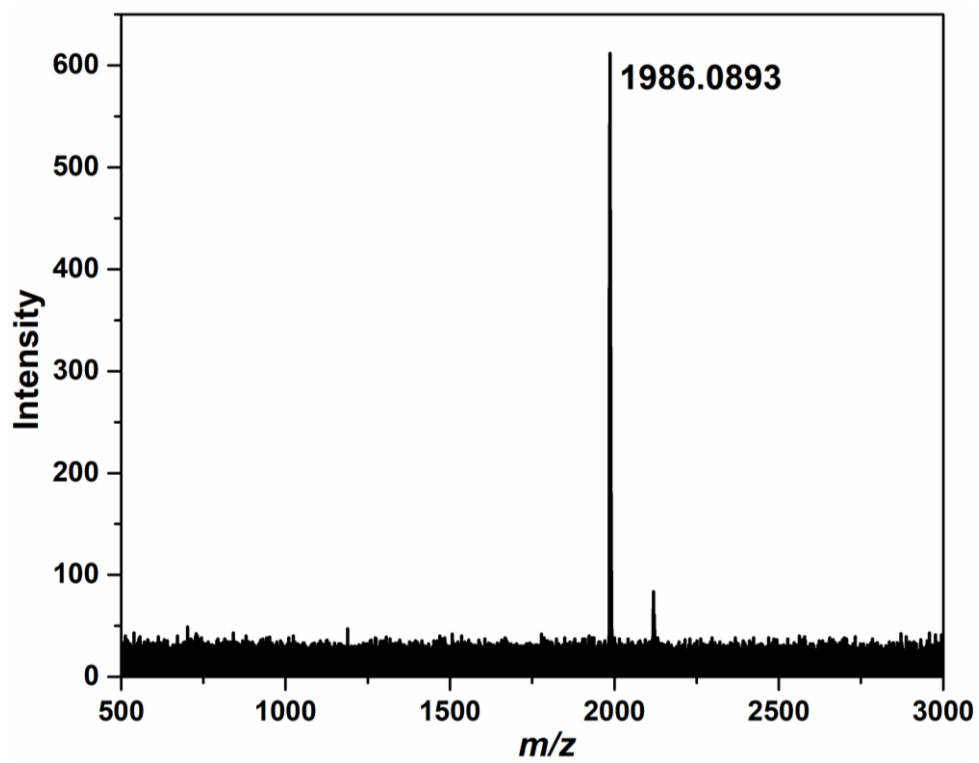
S5: ^1H - ^1H COSY spectrum of **3** in $\text{THF-}d_8$ at 198 K



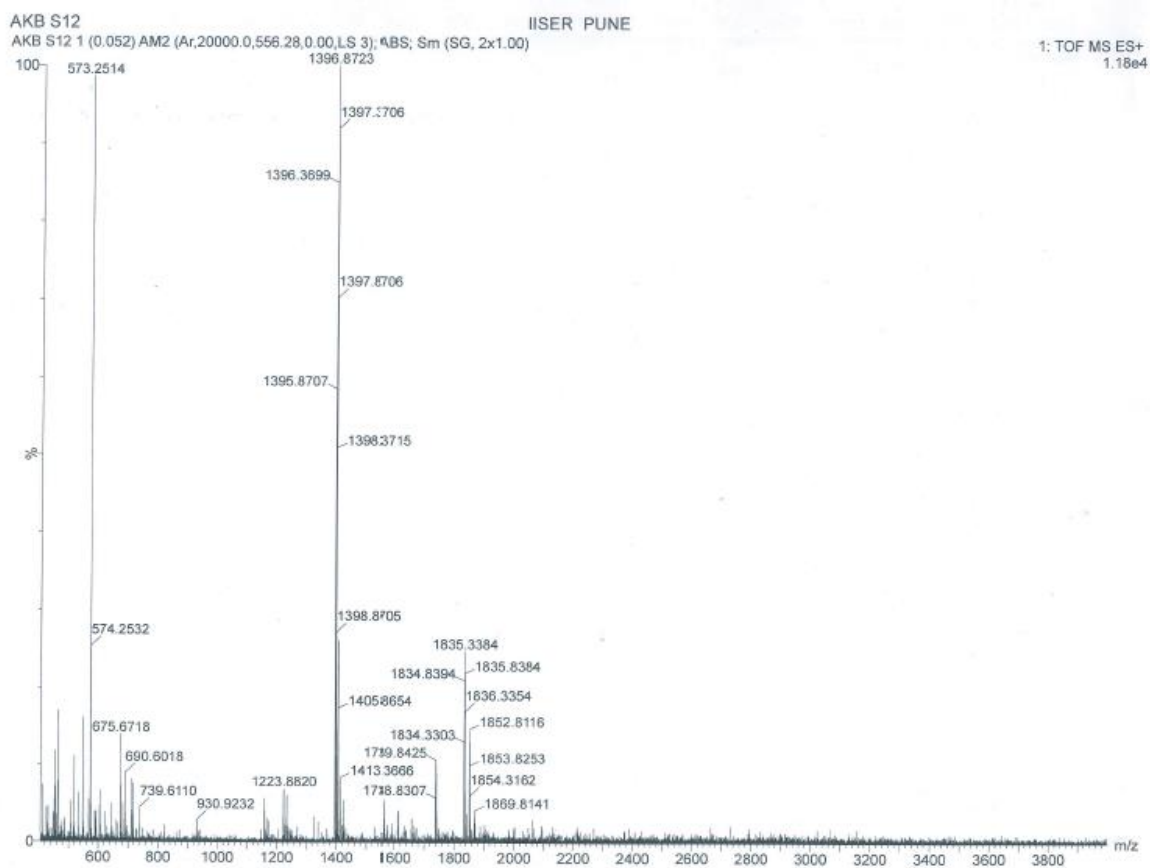
S6: The steady state absorption spectra (blue line) of **3** recorded in CHCl_3 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.



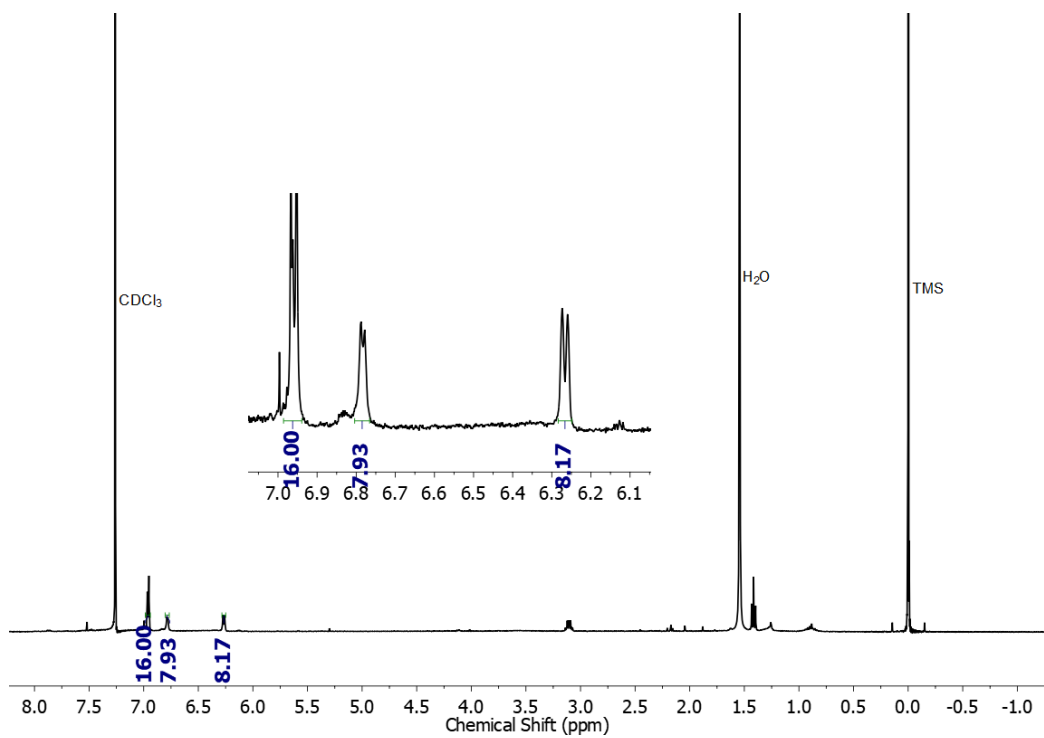
S7: Steady state absorption spectra (blue line) of **3** (dication) recorded in CHCl_3 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.



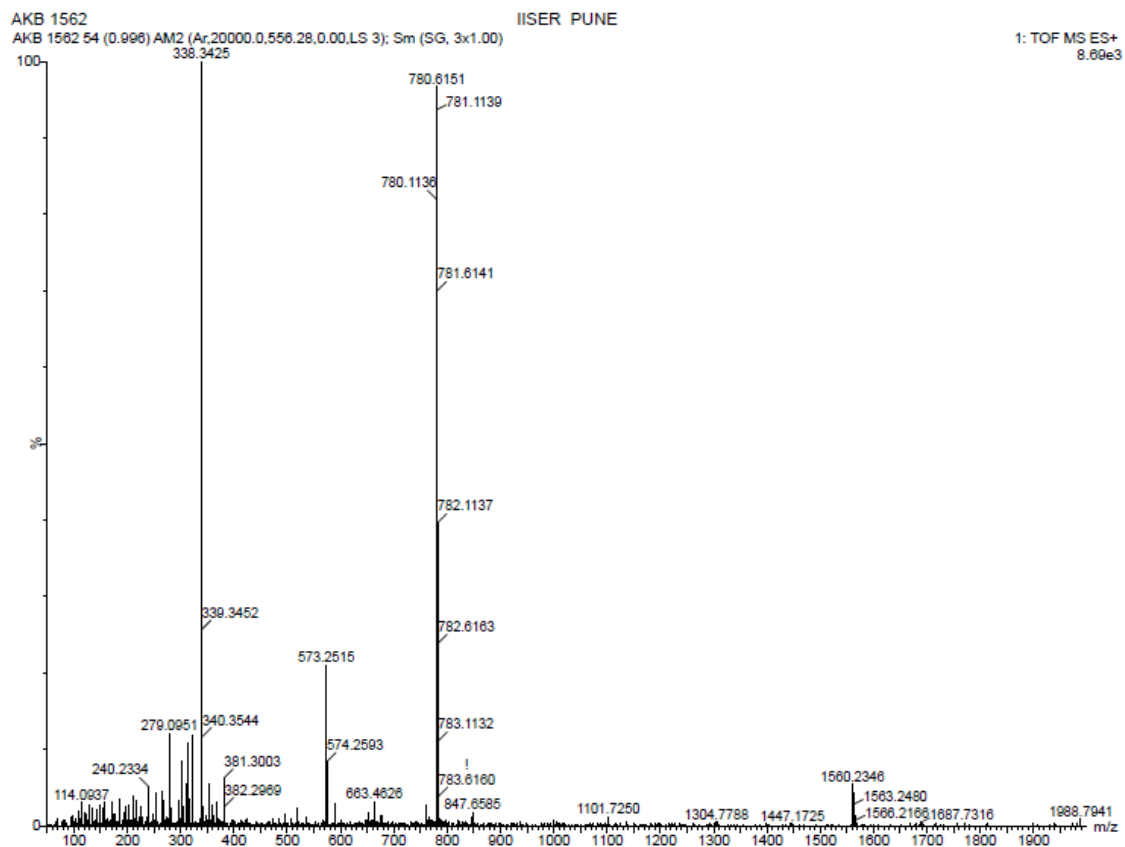
S8: MALDI-TOF/TOF mass spectrum of 5.



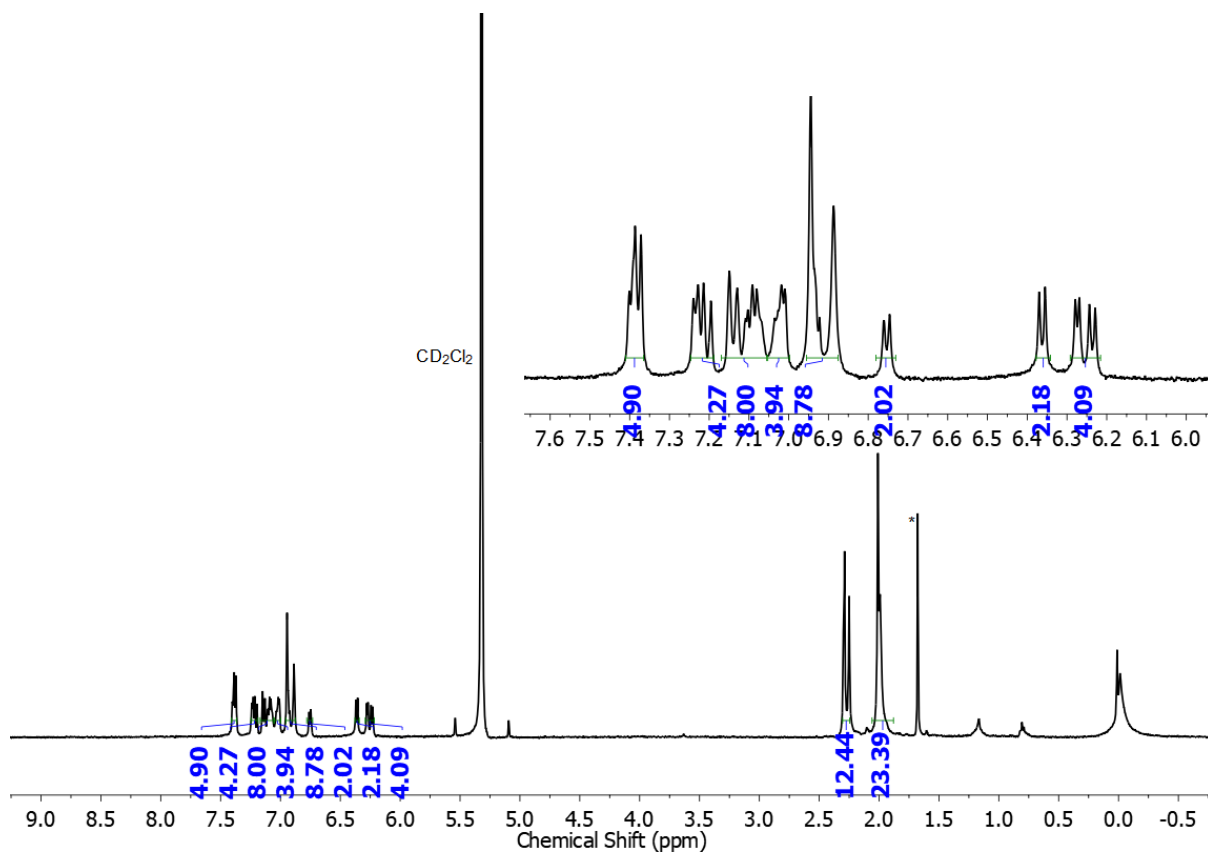
S9: High Resolution Mass Spectrum (HRMS) of **6**



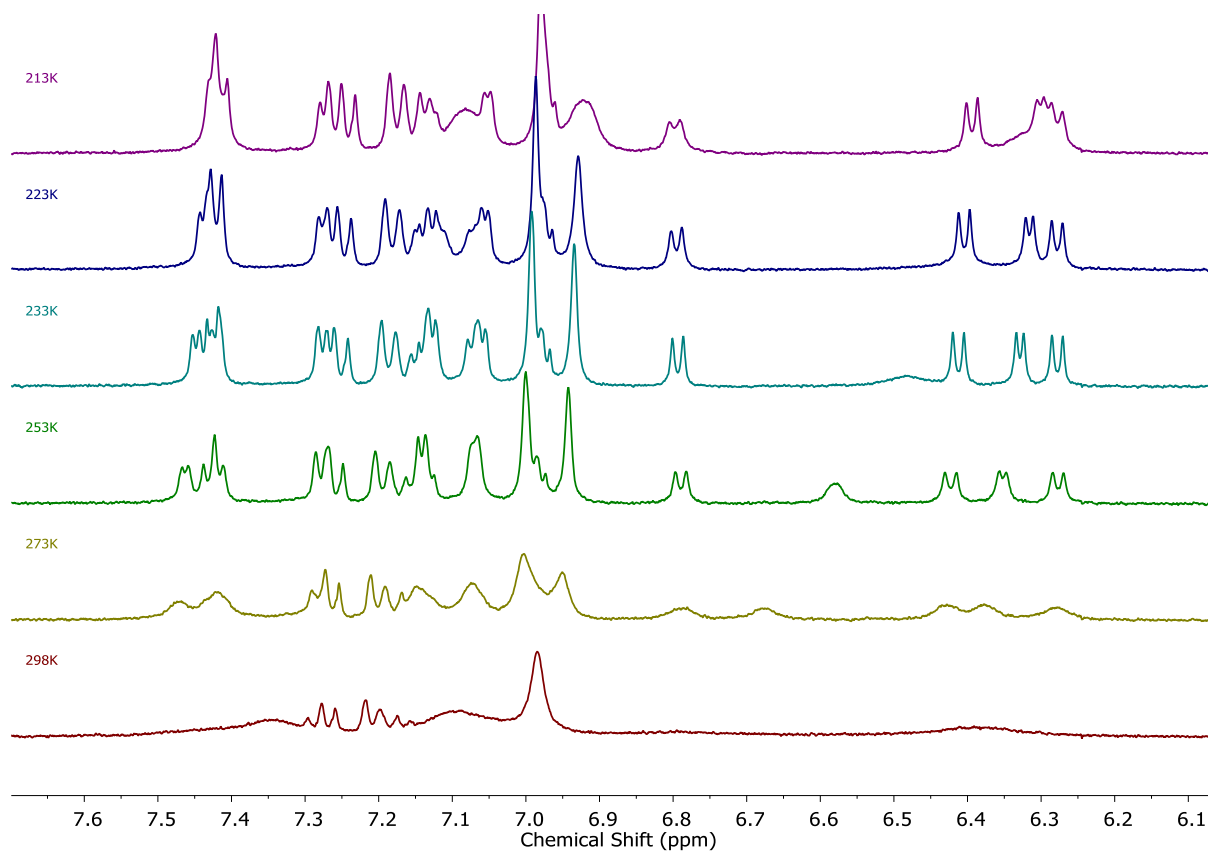
S10: ¹H NMR spectrum of **6** in CDCl₃ at 298 K



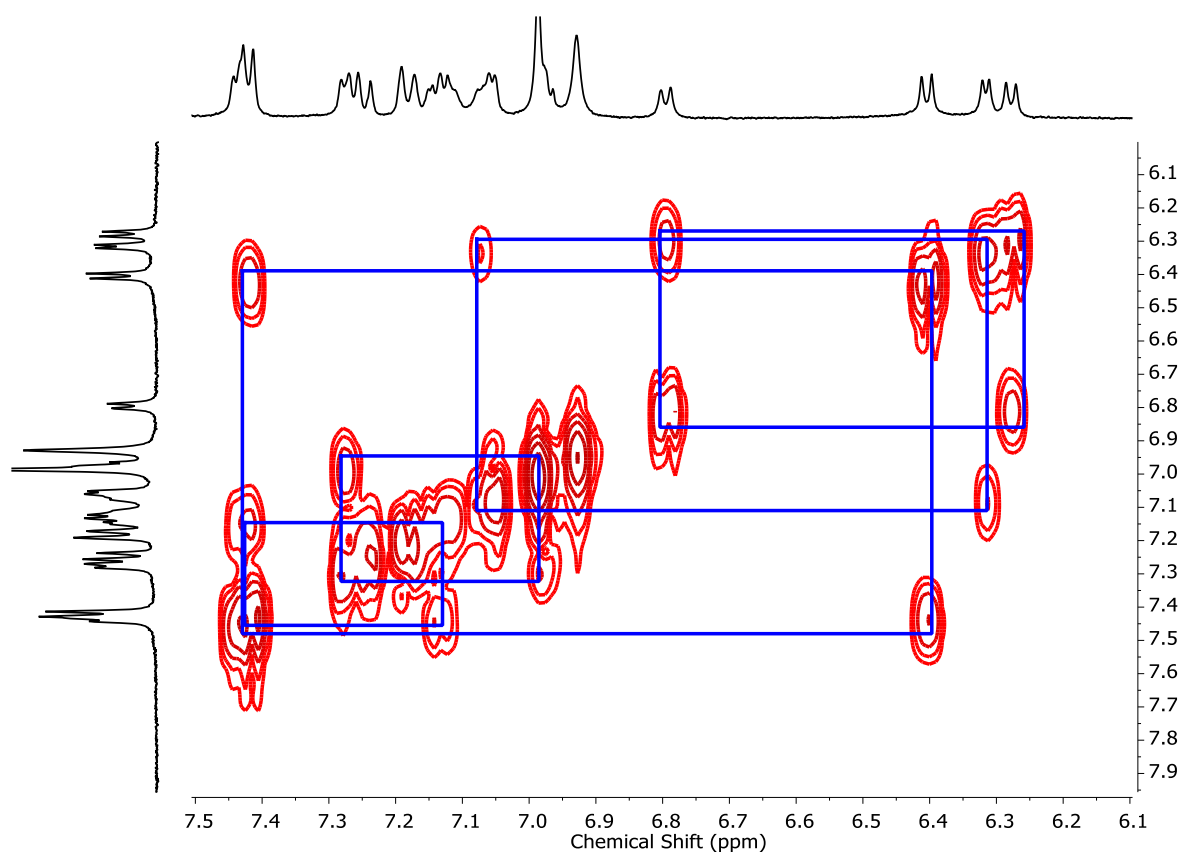
S11: High Resolution Mass Spectrum (HRMS) of 4



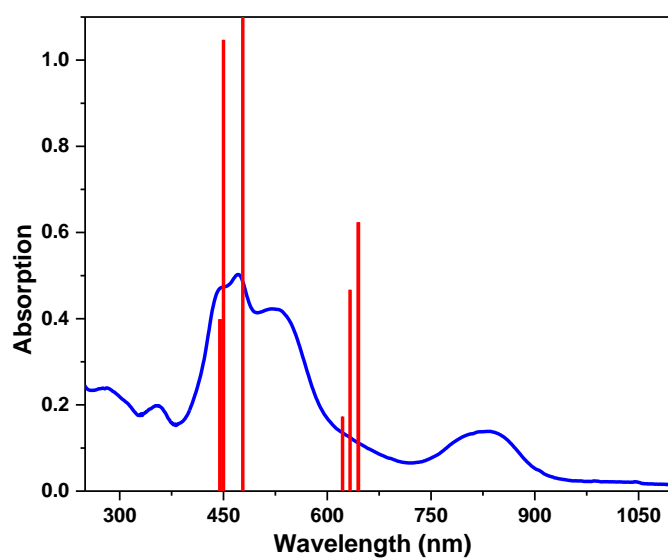
S12: ¹H NMR spectrum of **4** in Dichloromethane-*d*₂ at 223 K



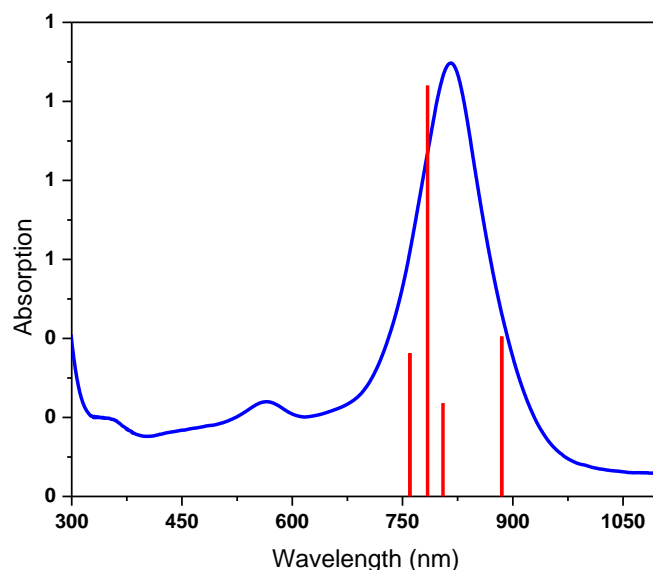
S13: Variable temperature ¹H NMR spectrum of **4** in Dichloromethane-*d*₂



S14: ^1H - ^1H COSY spectrum of **4** in Dichloromethane- d_2 at 223 K



S15: Steady state absorption spectra (blue line) of **4** recorded in CHCl_3 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.



S16: Steady state absorption spectra (blue line) of **4** (dication) recorded in CHCl_3 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.

References:

1. a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht, The Netherlands, 2005; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* 1990, 46, 194.
2. Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
3. Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R., Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **1996**, 118 (26), 6317-6318.