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**SUPPLEMENTARY INFORMATION**

# Strong absorber *vs* strong emitter in extended π-conjugated systems: a *carbo*-benzene - benzothiadiazole chromophore

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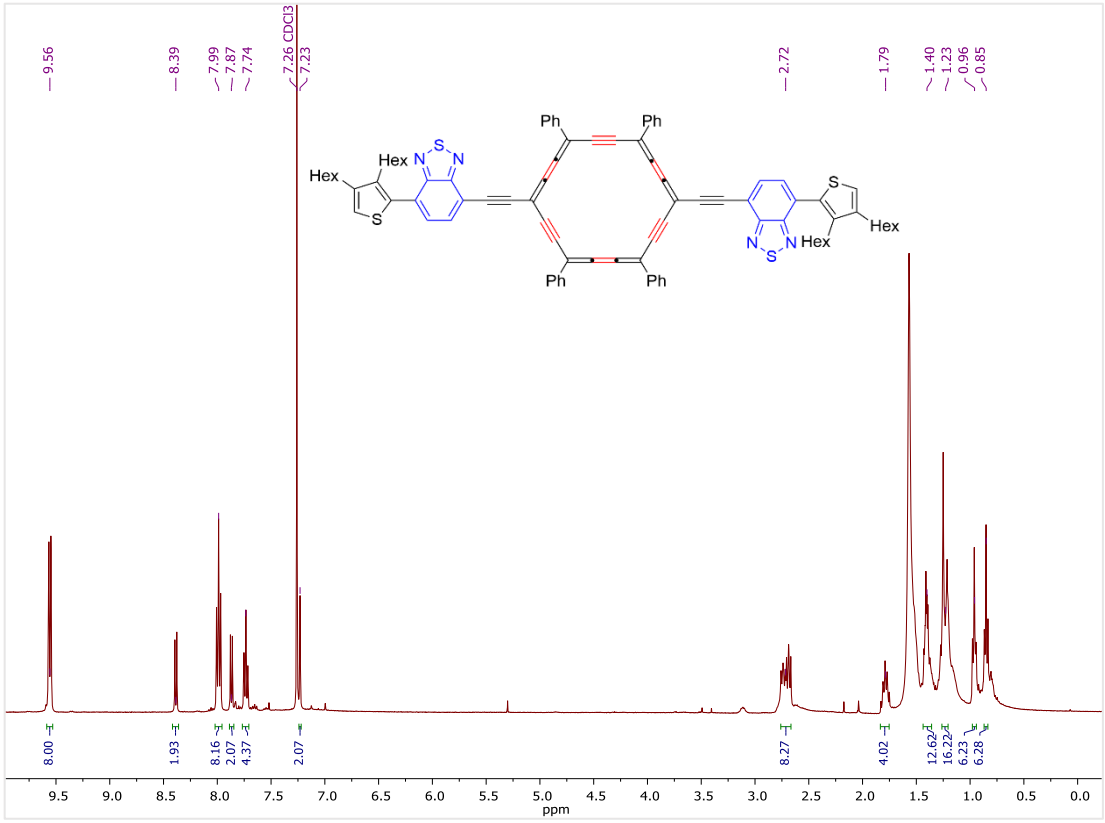
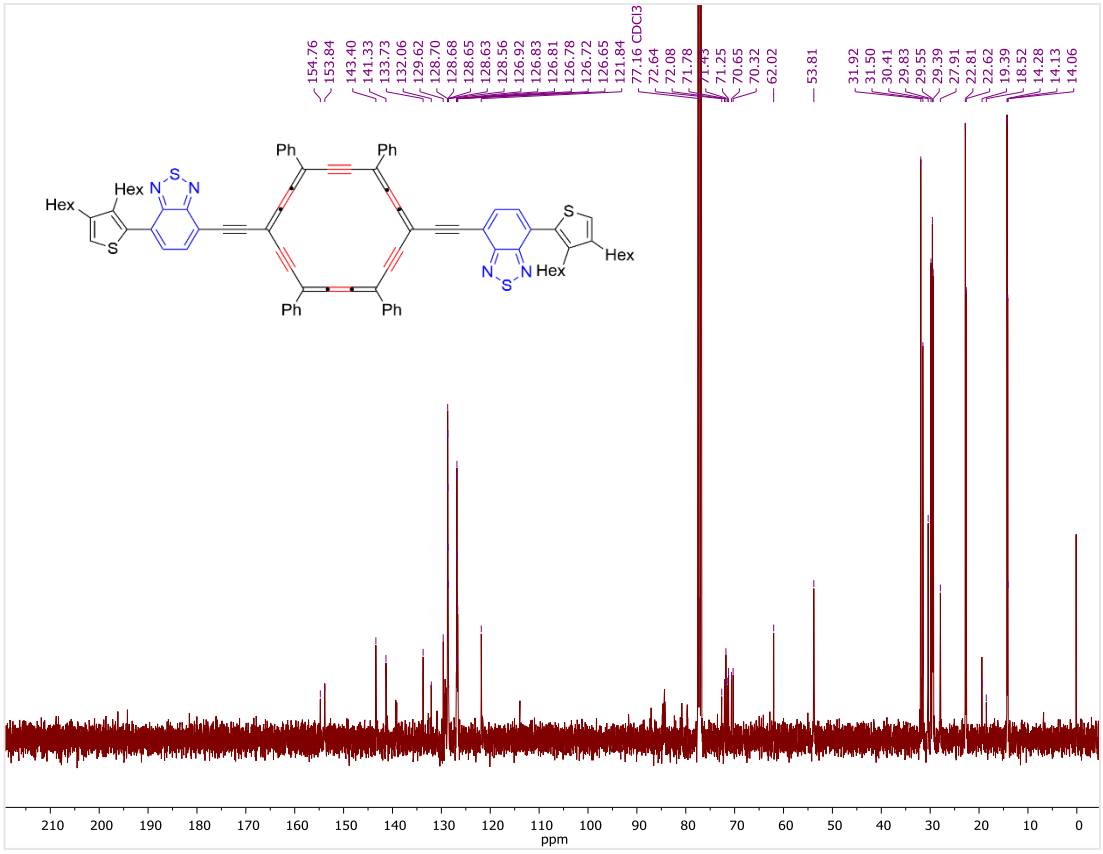
## Content

## 1- $^{1}H$ and $^{13}C$ spectra

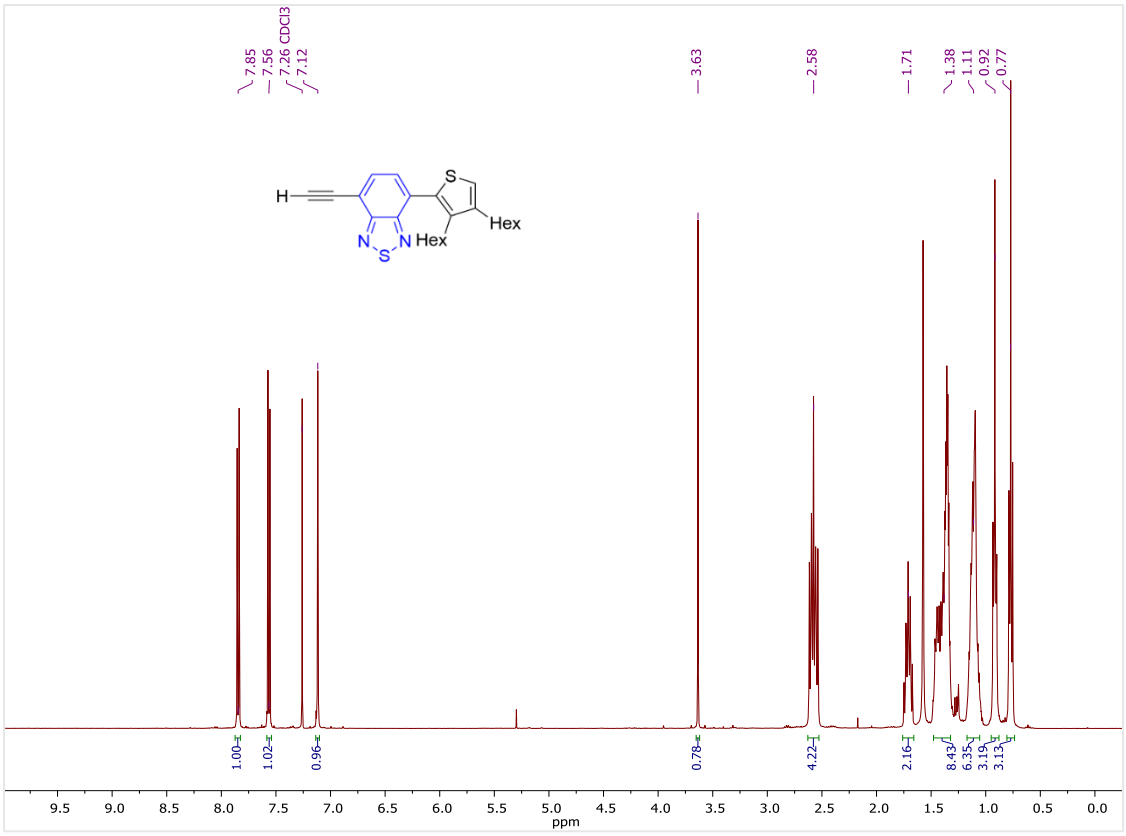
$^{1}H$ NMR spectrum of **2** ($CDCl_3$, 400.16 MHz)



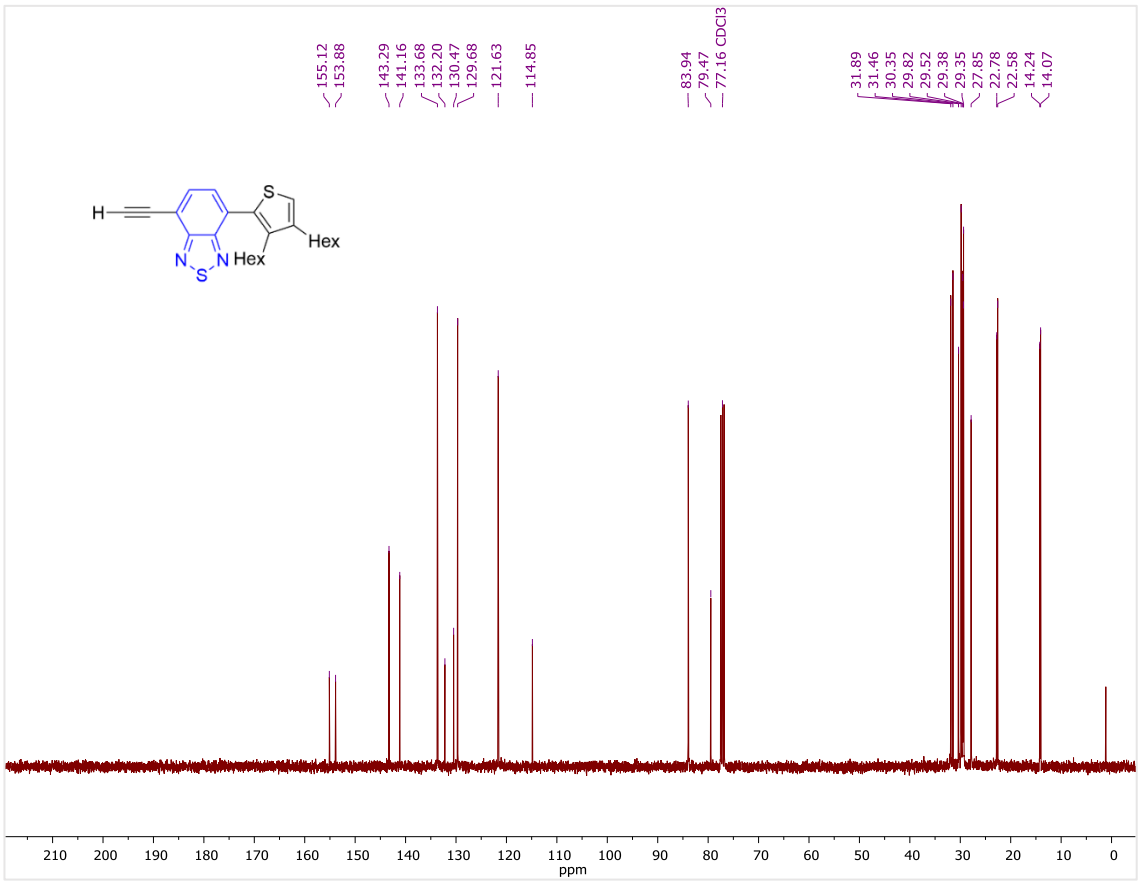

$^{13}C$ NMR spectrum of **2** ($CDCl_3$, 100.63 MHz)



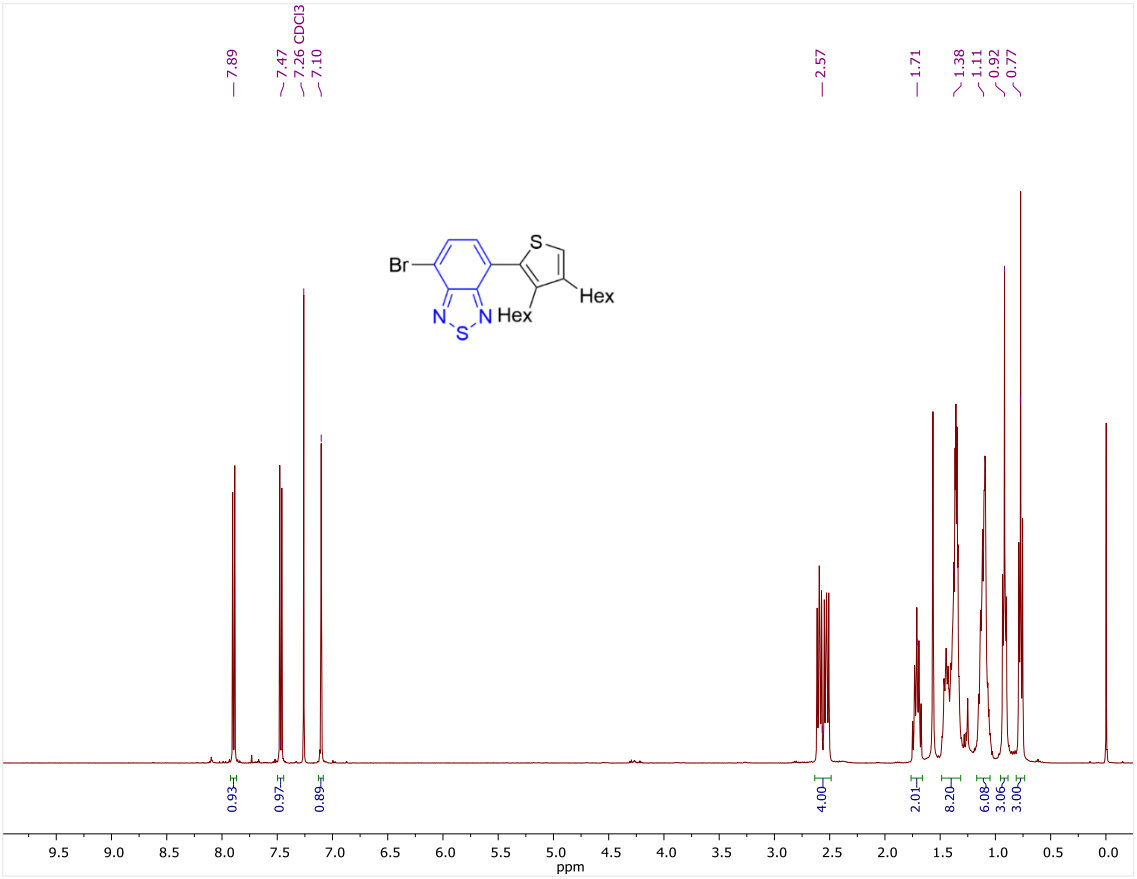
$^{1}$H NMR spectrum of **4** ($CDCl_3$, 400.16 MHz)



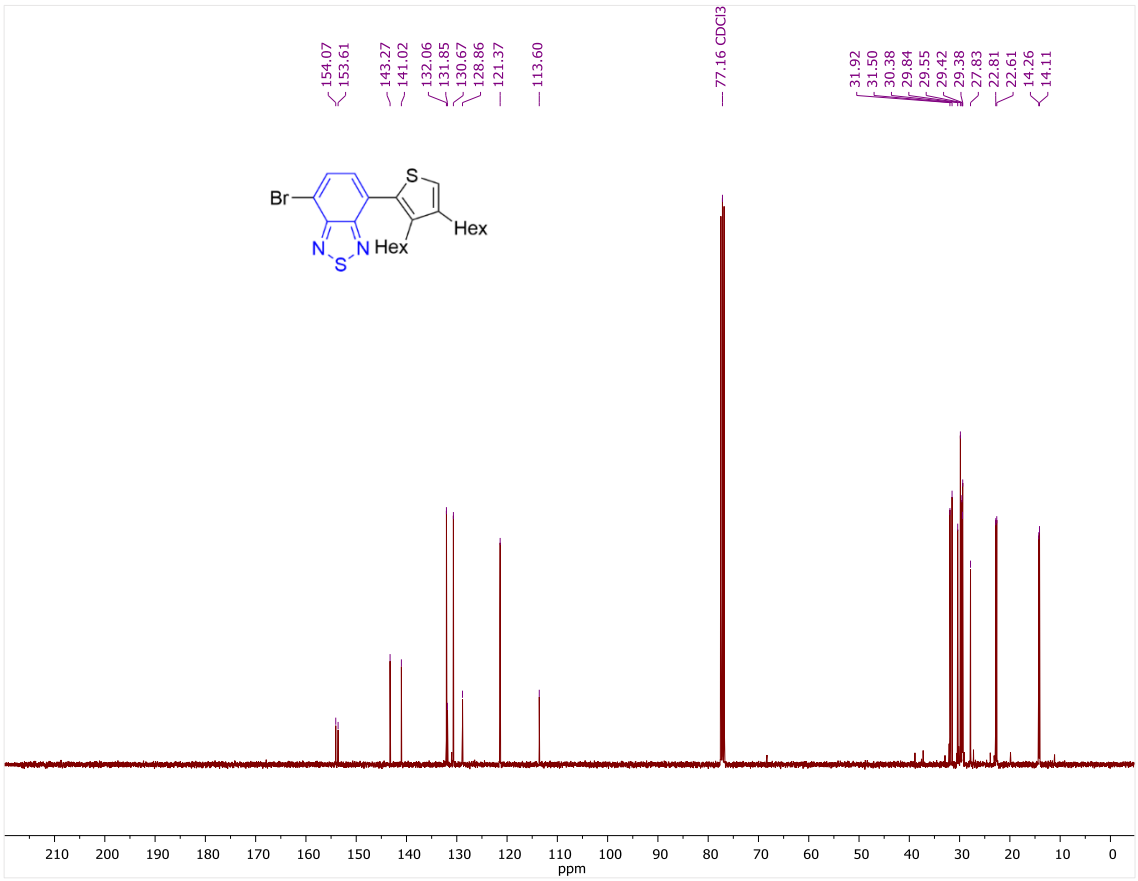

$^{13}$C NMR spectrum of **4** ($CDCl_3$, 100.63 MHz)



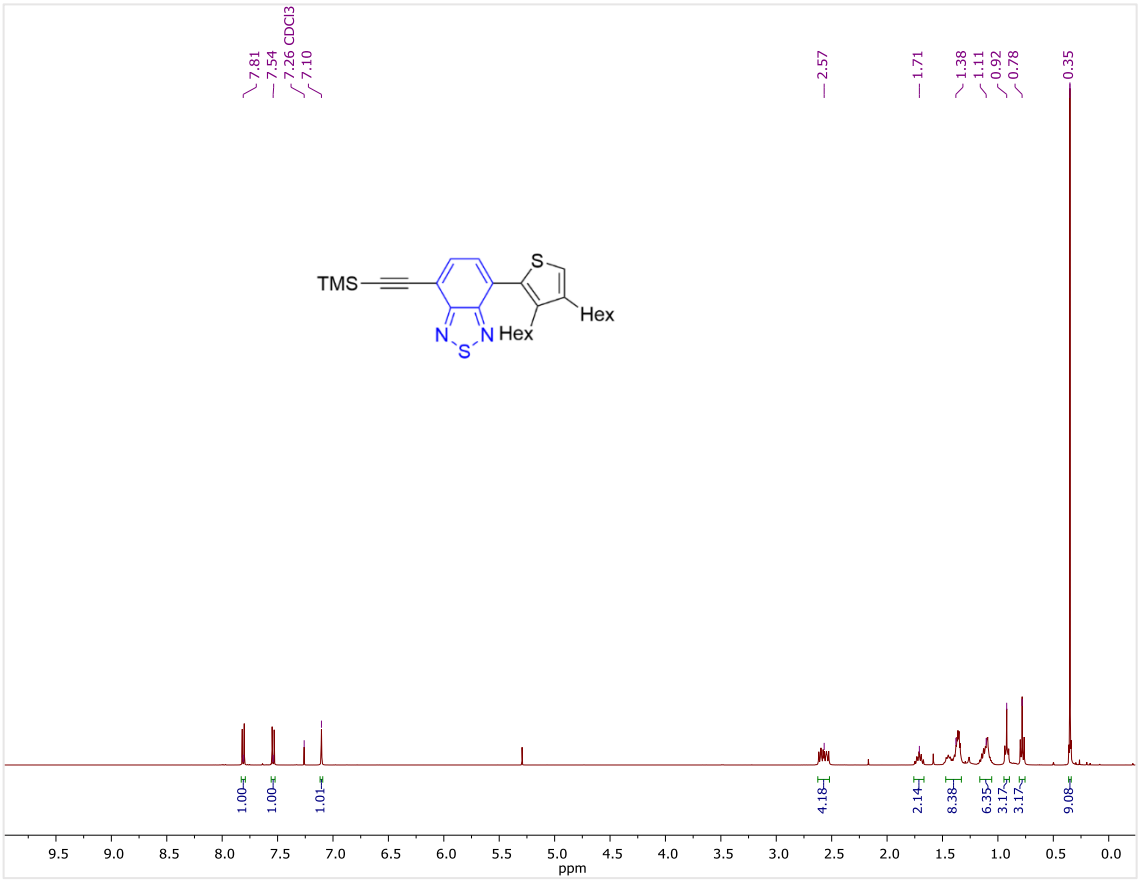
$^{1}$H NMR spectrum of **6** ($CDCl_3$, 400.16 MHz)



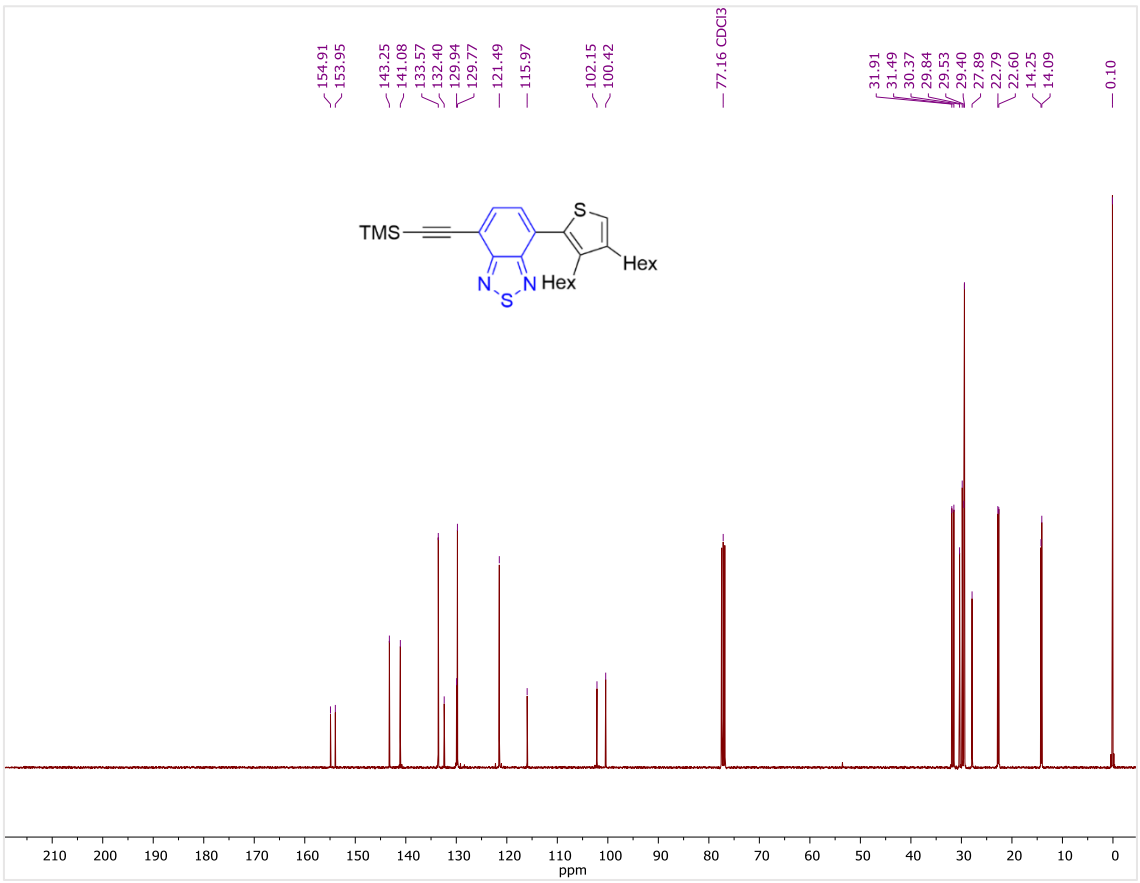

$^{13}$C NMR spectrum of **6** ($CDCl_3$, 100.63 MHz)



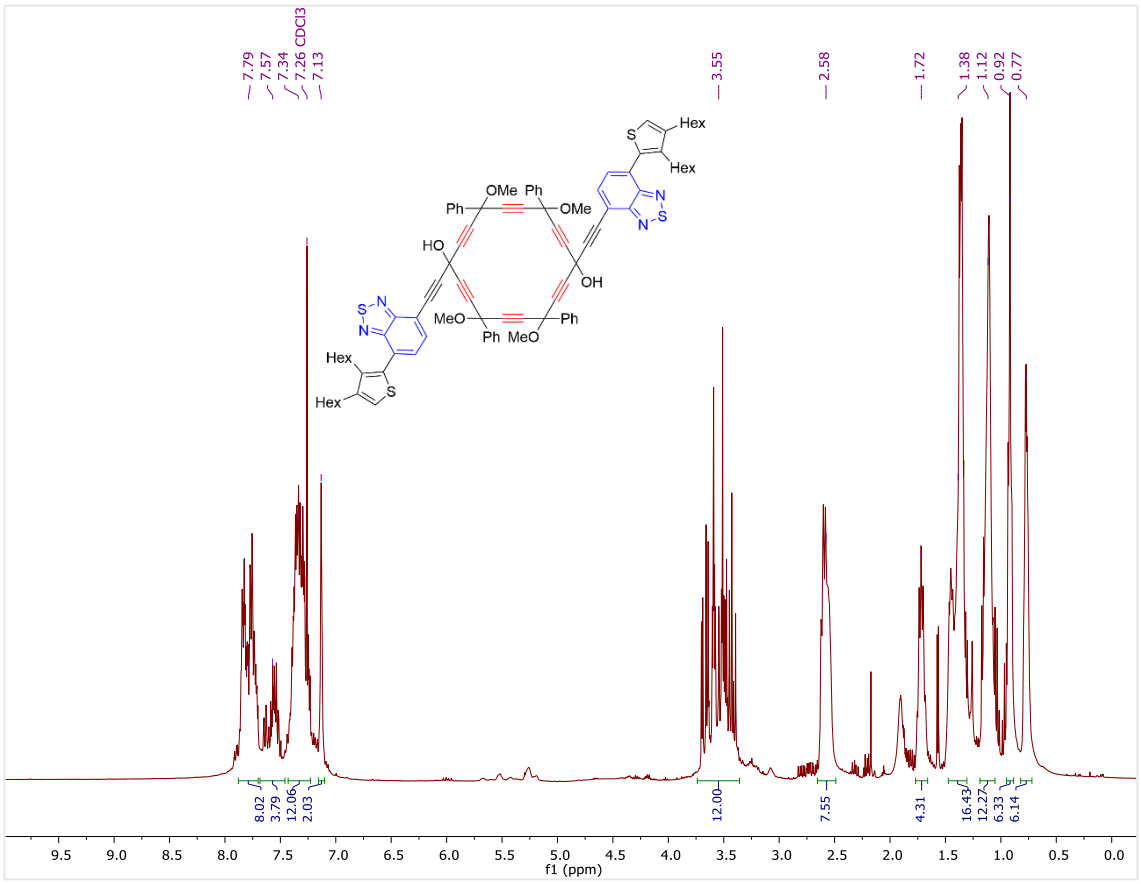
$^{1}$H NMR spectrum of **7** ($CDCl_3$, 400.16 MHz)



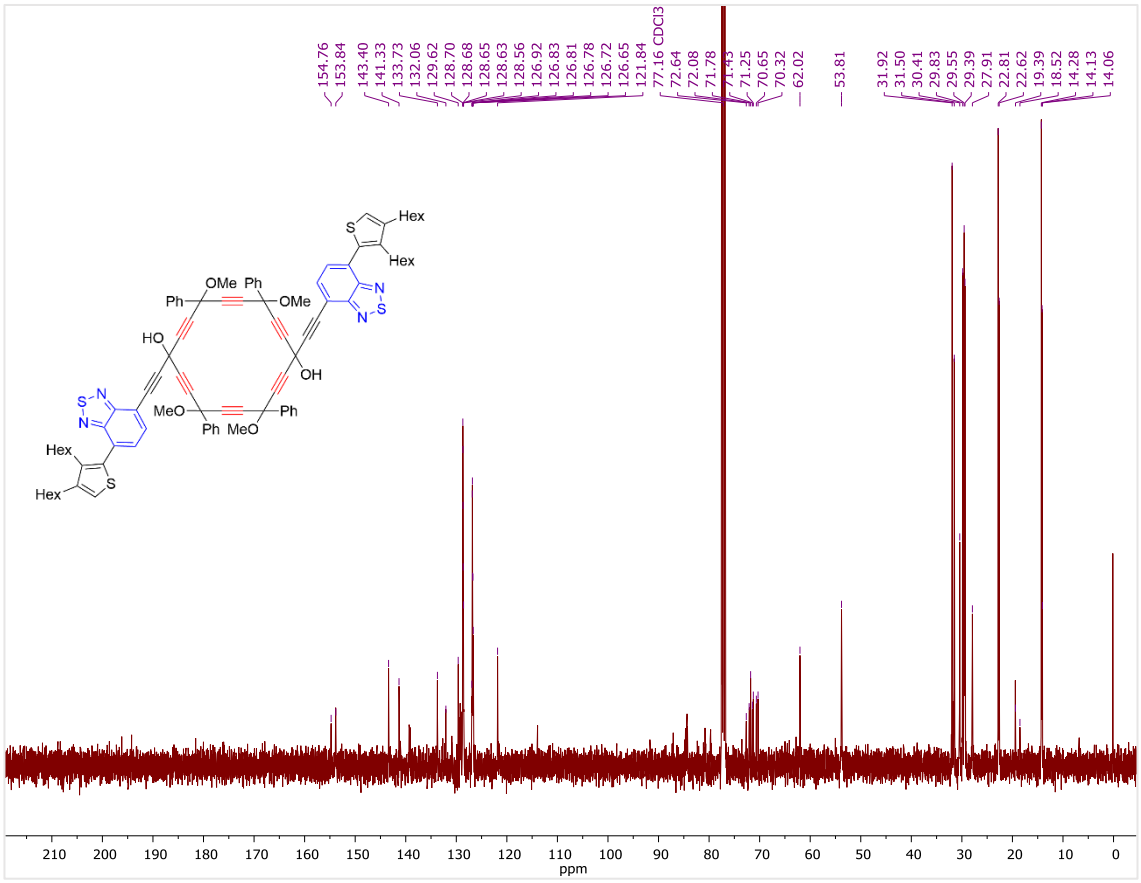

$^{13}$C NMR spectrum of **7** ($CDCl_3$, 100.63 MHz)



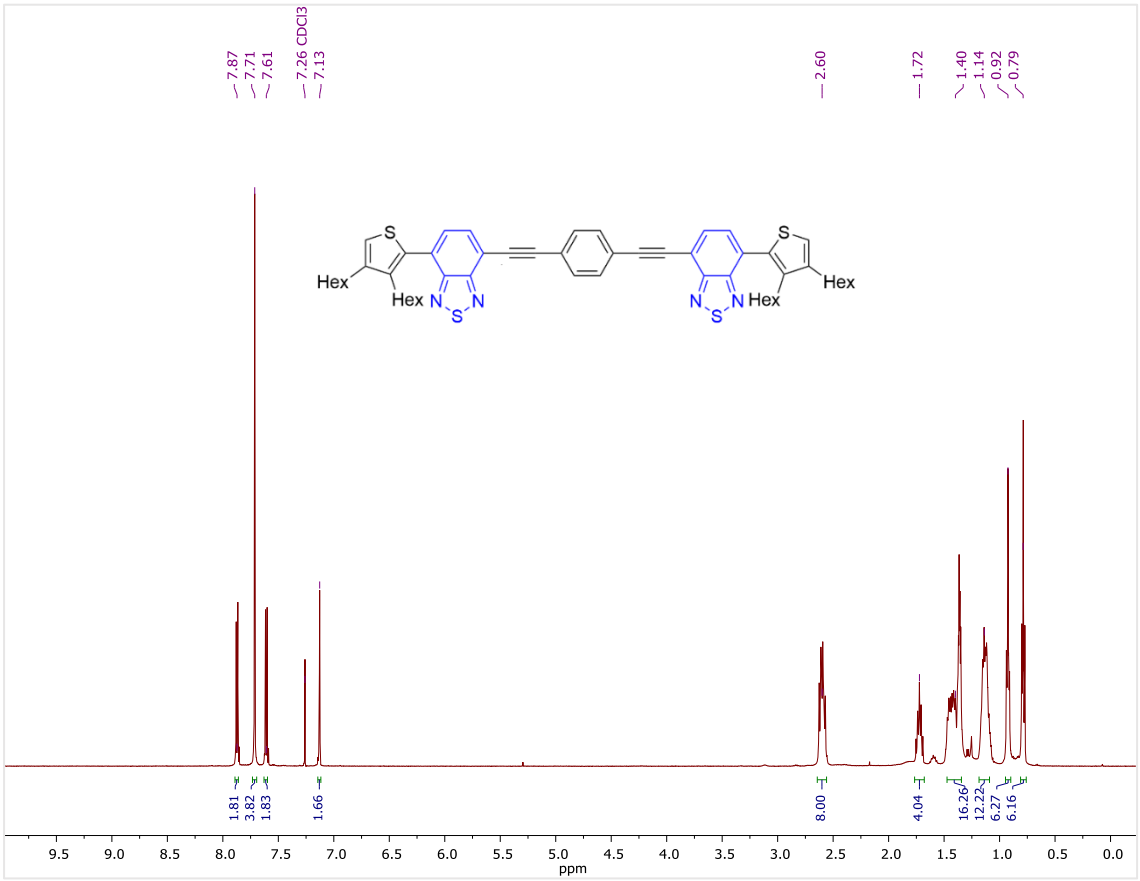
$^{1}$H NMR spectrum of **8** ($CDCl_3$, 400.16 MHz)



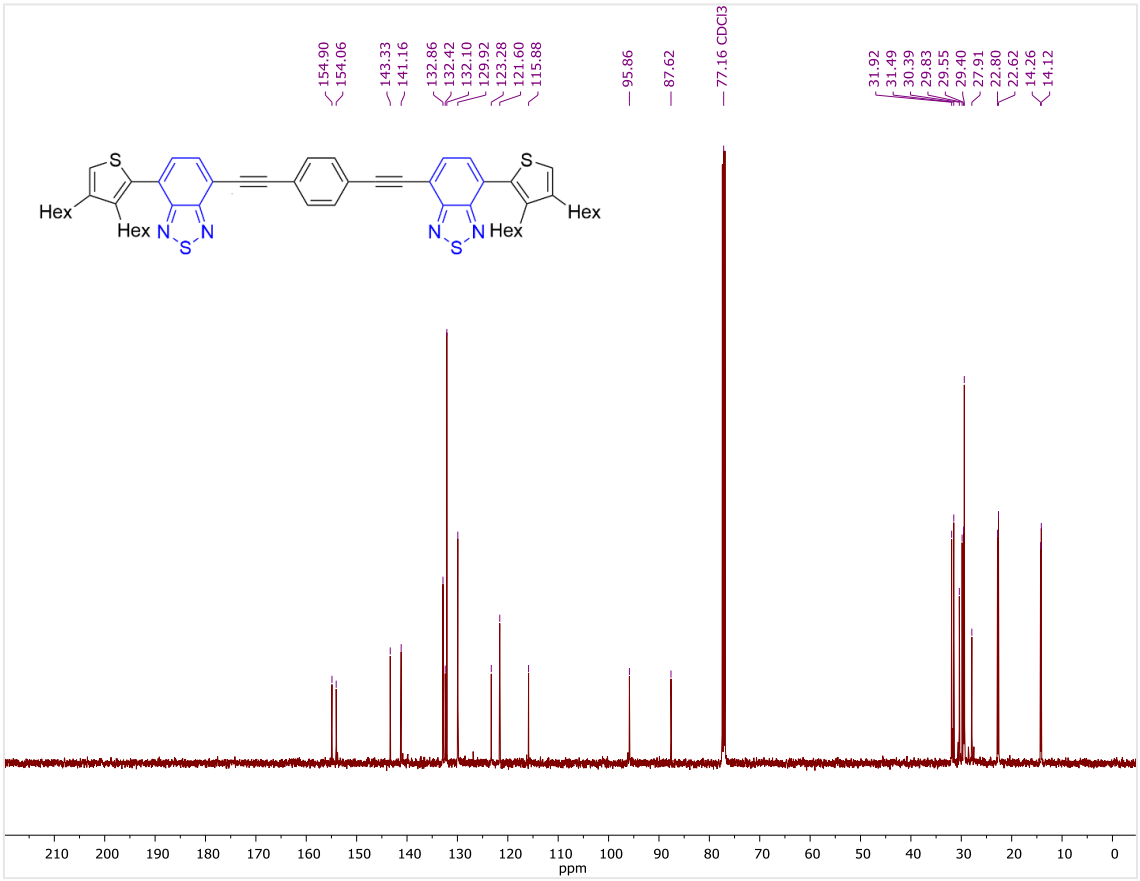

$^{13}$C NMR spectrum of **8** ($CDCl_3$, 100.63 MHz)



$^{1}$H NMR spectrum of **9** ($CDCl_3$, 400.16 MHz)




$^{13}$C NMR spectrum of **9** ($CDCl_3$, 100.63 MHz)



**2- Optical properties**

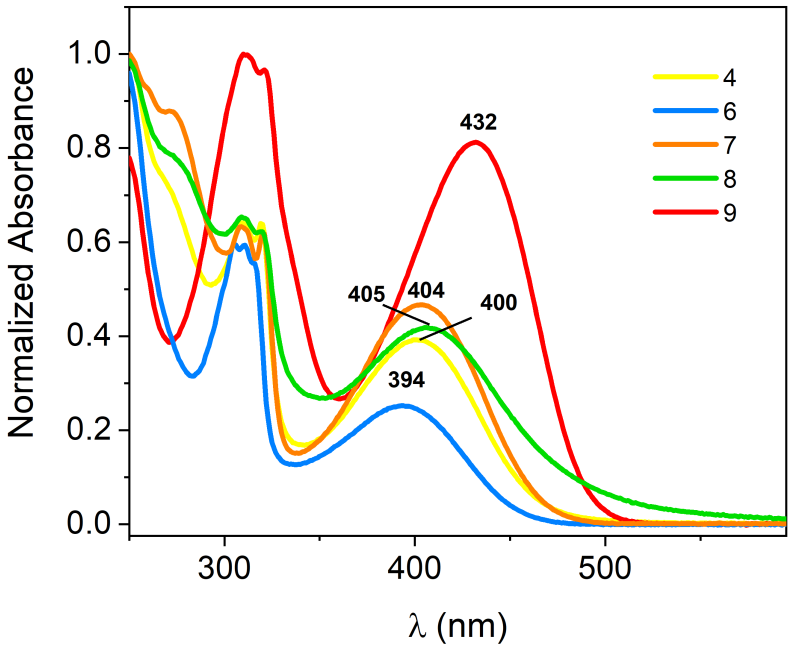



**Fig. S1.** Absorption spectra of the BTD-containing synthetic intermediates **4**, **6**, **7**, **8** and parent molecule **9** (see Schemes 2-3 in the main text) in chloroform solution.

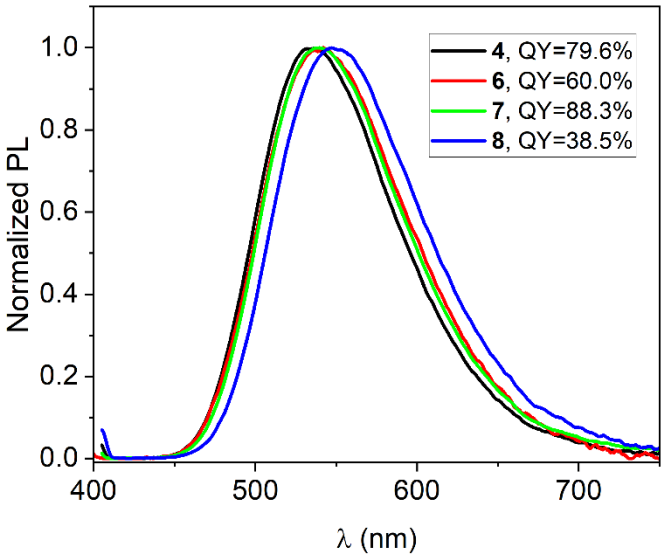



**Fig. S2.** PL spectra and quantum yield of fluorescence of the precursors **4**, **6**, **7** and **8**.

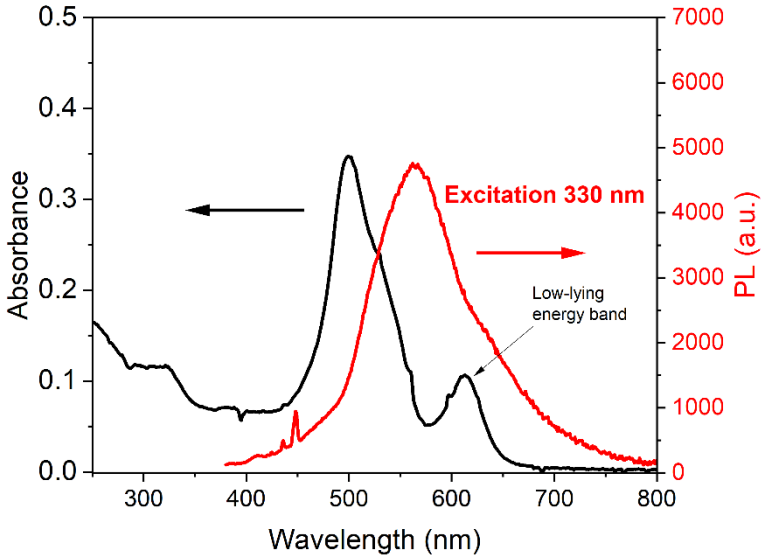



**Fig. S3.** Superimposed emission and absorption spectra of the thienyl-BTD-*carbo*-benzene **2** in chloroform solution, showing anomalous photoluminescence. The solution is highly diluted to reduce the internal effect (molecular reabsorption of emission). Due to the weak emission the excitation slit is quite open inducing the detection of straight light on the detector (see spurious spikes at approximately 450 nm)

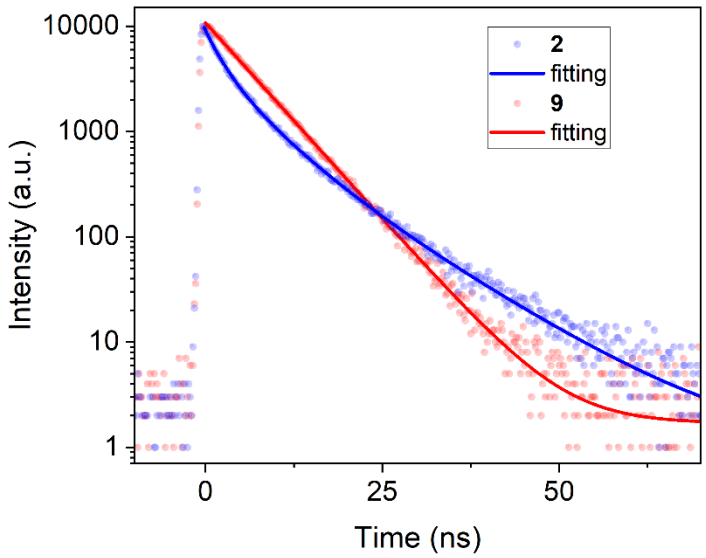



**Fig. S4.** Fitted data of PL decay measured by TCSPC.

**Table S1.** Fitting parameters for the PL decay obtained by TCSPC.

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + \ldots$$

| | | parent bz **9** | | cbz **2** | |
|---|---|---|---|---|---|
| $\tau_1$ | $A_1$ | 5.82 ns | 11190.70 | 2.07 ns | 5318.78 |
| $\tau_2$ | $A_2$ | | | 5.44 ns | 3790.37 |
| $\tau_3$ | $A_3$ | | | 10.88 ns | 1230.24 |

Average lifetime :

$$\langle \tau \rangle = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$$

## 3- DFT calculations

### 3.1. Computational methods for geometry optimization

Static DFT calculations have been performed at the GGA level with the program Firefly v. 8.1.1,[1] using the B3PW91 functional of Becke, Perdew and Wang.[2] with the 6-31G(d,p) basis set for H, C, and S atoms.[3]

Geometry optimizations of truncated models of the *carbo*-benzene ("cbz") **2**, benzenic parent ("bz") **9**, and their respective radical cations ($\mathbf{2}^{+}$, $\mathbf{9}^{+}$) and anions ($\mathbf{2}^{-}$, $\mathbf{9}^{-}$) were carried out under $C_i$ symmetry constraint, the characterization of the equilibrium stationary points being performed by analytical frequency calculations. Total energies are given without zero-point correction.

Molecular orbitals and electron density maps (Table S3 and Fig. S5) were edited using the interface program MacMolPlt, v. 7.7. [4]

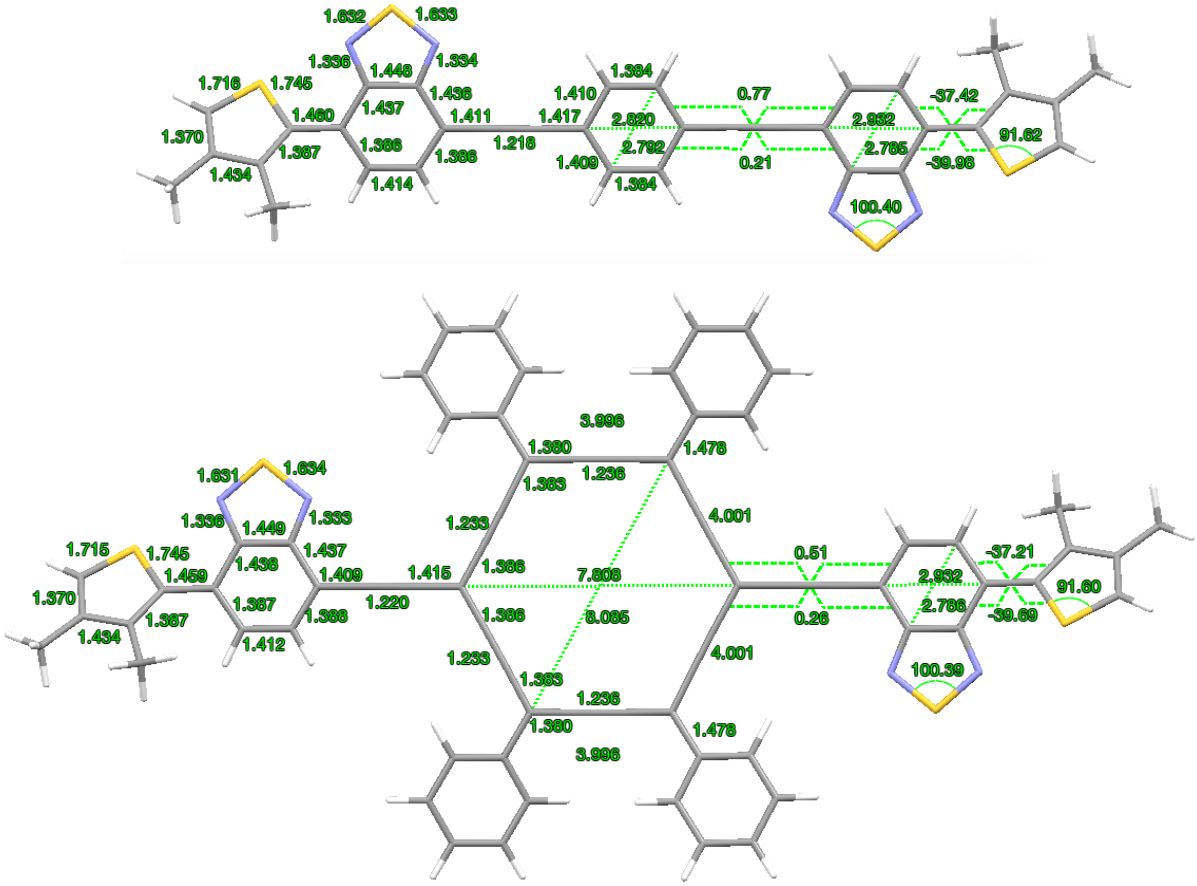



**Fig. S5.** Geometrical data of the calculated equilibrium structure of **2** (*bottom*) and **9** (*top*). Bond lengths in Å, dihedral bond angles in degrees.

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1 a) A. A. Granovsky, *Firefly version 8,* http://classic.chem.msu.su:gran:firefly:index.html) which is partially based on the GAMESS (US) source code; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.* 1993, **14**, 1347-1363.

2 (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652. (b) J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244-13249.

3 (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724. (b) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comp. Chem.* 1983, **4**, 294-301.

4 B. M. Bode and M. S. J. Gordon, *J. Mol. Graphics and Modeling* 1998, **16**, 133-138.

### 3.2. Chemical potential, hardness and electrophilicity

According to conceptual DFT, [5] the chemical potential $\mu$ of a *N*-electron system of total electronic energy *E* is defined as the first derivative of *E vs N* at a fixed external (nuclear) potential *v*: $\mu = (\partial E/\partial N)_v$; it is identified to the negative of electronegativity $\chi$ ($\mu = -\chi$). The molecular hardness $\eta$ is defined as the corresponding second derivative: [6] $\eta = (\partial^2 E/\partial N^2)_v$ (on the basis of the Taylor expansion of *E vs n*, a factor 1/2 was originally proposed in the alternative definition $\eta' = 1/2\ (\partial^2 E/\partial N^2)_v$). [7] In numerical applications, $\mu$ (the Fermi level) and $\eta$ (the HOMO-LUMO gap) are calculated by finite difference formulas, which, at the first order, are equivalent to the Pearson's definition of electronegativity and twice the hardness, within the Koopmans' approximation for ionization potential and electron affinity: [8]

$$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_v \cong \frac{1}{2}(\varepsilon_L + \varepsilon_H), \qquad \eta \equiv \left(\frac{\partial^2 E}{\partial N^2}\right)_v \cong \varepsilon_L - \varepsilon_H$$

where $\varepsilon_H$ and $\varepsilon_L$ denote the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.

Electrophilicity $\omega$ is the ratio of the chemical potential squared to twice the hardness; a principle of electrophilicity equalization of the constituting atoms within a molecule has been proposed: [9]

$$\omega = \frac{\mu^2}{2\eta}$$

Results are listed in Table S2.

**Table S2.** HOMO, LUMO and electronic indices in the Koopmans' approximation (energies in Hartree).

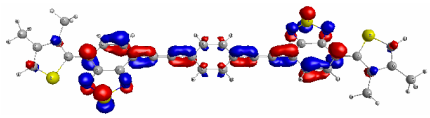
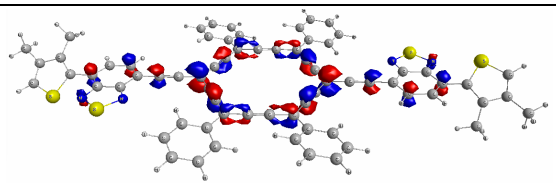
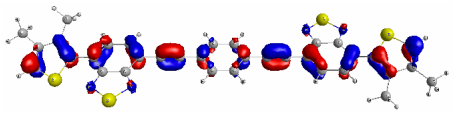
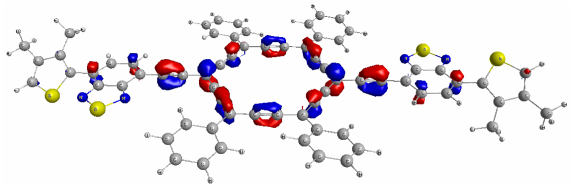
| Energies in a.u. | HOMO (possibly SOMO) $\varepsilon_H$ | LUMO or SOMO for radicals $\varepsilon_L$ | chemical potential $\mu$ (Pearson value) | chemical hardness $\eta$ (Pearson value) | electrophilicity $\omega$ |
|---|---|---|---|---|---|
| parent bz **9** | -0.2951 | -0.1951 | -0.2451 (-0.1482) | 0.1000 (0.0786) | 0.3004 (0.140) |
| parent bz cation **9**$^+$ | -0.2863 | -0.2863 | -0.2863 | 0 | - |
| parent bz anion **9**$^-$ | -0.0372 | -0.0372 | -0.0372 | 0 | - |
| cbz **2** | -0.1897 | -0.1206 | -0.1551 (-0.1544) | 0.0691 (0.0659) | 0.1742 (0.181) |
| cbz cation **2**$^+$ | -0.2649 | -0.2649 | -0.2649 | 0 | - |
| cbz anion **2**$^-$ | -0.0693 | -0.0693 | -0.0693 | 0 | - |

5 R. G. Parr, L. von Szentpaly and S. Liu, *J. Am. Chem. Soc.* 1999, **121**, 1922-1924
6 P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev*. 2003, **103**, 1793-1873
7 a) R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press: New York, 1989; b) R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, *J. Chem. Phys*. 1978, **68**, 3801-3807; c) R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc*. 1983, **105**, 7512-7516.
8 T. Koopmans, *Physica* 1934, **1**, 104-113.
9 P. K. Chattaraj, S. Giri and S. Duley, *J. Chem. Phys. Lett*. 2010, **1**, 1064-1067.

### 3.4. Frontier orbitals of the neutral molecules

Eigenvalues and spatial distributions of the HOMO and LUMO are listed in Table S3.

**Table S3.** Frontier molecular orbitals, HOMO and LUMO, of **2** and **9** (energies in a.u.).

| | parent bz **9** | cbz **2** |
|---|---|---|
| LUMO |  |  |
| | *E*(LUMO, no 160, Au) = -0.1951 au | *E*(LUMO, no 276, Ag) = -0.1206 au |
| HOMO |  |  |
| | *E*(HOMO, no 159, Ag) = -0.2951 au | *E*(HOMO, no 275, Au) = -0.1897 au |

### 3.3. Adiabatic ionization energy and electron affinity in the Koopman's approximation

#### 3.3.1. Adiabatic ionisation energy

*IE*(**9**) = *E*(**9**$^{+}$) – *E*(**9**) = -3119.53271 – (-3119.75946) = 0.22675 au

*IE*(**2**) = *E*(**2**$^{+}$) – *E*(**2**) = -4500.1185511063 – (-4500.3325115314) = 0.21396 au

#### 3.3.2. Adiabatic electron affinity

*EA*(**9**) = – [*E*(**9**$^{-}$) – *E*(**9**)] = –[-3119.82902– (-3119.75946)] = 0.06957 au

*EA*(**2**) = – [*E*(**2**$^{-}$) – *E*(**2**)] = –[-4500.4273744738 – (-4500.3325115314)] = 0.09486 au

### 3.4 Electron density and molecular electrostatic potential

As shown in Fig. S6, the electron density of **2** and **9** concentrates in the vicinity of the formal triple bonds of the Lewis structures while the MESP becomes more negative, as expected (sp-hybridized C atoms are indeed generally considered as more electronegative). The S atoms of the thiophene and BTD rings appear with the same electronegativity, as expected as well.

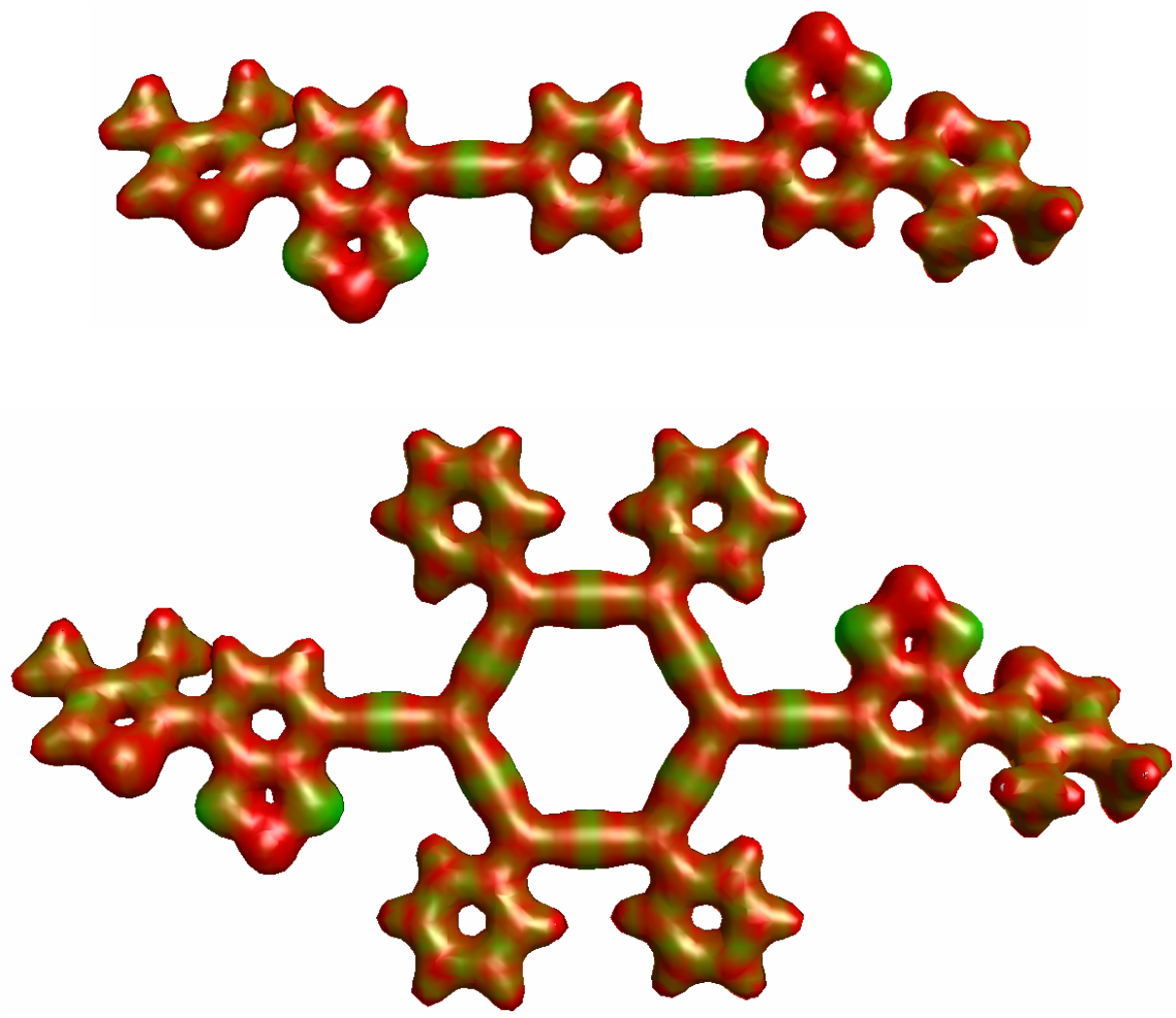


**Fig. S6.** Electron density map of **2** (*bottom*) and **9** (*top*), contour value = 0.07; color code: proportional to the molecular electrostatic potential, negative –> green, positive –> red (maximum MESP value mapped: 0.30 au).

### 3.5. Cartesian coordinates and total energy in the calculated equilibrium geometry in the gas phase

| | *x* | *y* | *z* |
|---|---|---|---|
| parent bz **9** ($C_i$ symmetry)<br><br>NUCLEAR ENERGY = 4442.8837025802<br>ELECTRONIC ENERGY = -7562.6431586706<br>TOTAL ENERGY = -3119.7594560904 | | | |
| C | 6.0 | 1.3454276232 | -0.0625198059 | -0.3696944212 |
| C | 6.0 | 0.6777919848 | -1.2357273453 | 0.0361559449 |
| C | 6.0 | -0.6797281701 | -1.1500916289 | 0.4051080675 |
| H | 1.0 | 2.3907112824 | -0.1233402695 | -0.6545489047 |
| H | 1.0 | -1.2003805866 | -2.0490430980 | 0.7189654801 |
| C | 6.0 | 1.9715764388 | -3.5306434236 | 0.0943996553 |
| C | 6.0 | 1.3644822832 | -2.4746082083 | 0.0706920293 |
| C | 6.0 | 2.0916093363 | -5.9441563582 | 0.5283129118 |
| C | 6.0 | 2.7991016951 | -7.1674663540 | 0.5719326244 |
| C | 6.0 | 4.1272482546 | -7.2994974759 | 0.1972147696 |
| C | 6.0 | 4.7733911475 | -6.0854199595 | -0.2206295582 |
| C | 6.0 | 4.0583484707 | -4.8263400701 | -0.2568962818 |
| C | 6.0 | 2.6755073219 | -4.7536246303 | 0.1246424998 |
| H | 1.0 | 1.0521900119 | -5.9327083070 | 0.8404748821 |
| H | 1.0 | 2.2765361368 | -8.0397847015 | 0.9488495471 |
| N | 7.0 | 6.0457082967 | -5.9759372906 | -0.6128116181 |
| N | 7.0 | 4.8013981604 | -3.7984789414 | -0.6695066489 |
| S | 16.0 | 6.2857799749 | -4.4042909997 | -0.9809291709 |
| S | 16.0 | 6.4680072075 | -8.6904885506 | 0.7997767878 |
| C | 6.0 | 6.4568253511 | -10.4001767103 | 0.6587802810 |
| C | 6.0 | 4.8189963034 | -8.5840919583 | 0.2390777058 |
| C | 6.0 | 5.2700211662 | -10.8855075614 | 0.1771032418 |
| C | 6.0 | 4.3188772226 | -9.8405534970 | -0.0675092156 |
| C | 6.0 | 4.9999891045 | -12.3387090183 | -0.0792942036 |
| C | 6.0 | 2.9654065654 | -10.1227986066 | -0.6524484356 |
| H | 1.0 | 7.3405591602 | -10.9682401944 | 0.9195138006 |
| H | 1.0 | 5.8479214958 | -12.9556520267 | 0.2282065381 |
| H | 1.0 | 4.1165366684 | -12.6883717684 | 0.4669500065 |
| H | 1.0 | 4.8178938249 | -12.5336783506 | -1.1429701636 |
| H | 1.0 | 3.0382320670 | -10.8821415542 | -1.4380191477 |
| H | 1.0 | 2.5185071868 | -9.2285335117 | -1.0918610384 |
| H | 1.0 | 2.2653040202 | -10.5116950559 | 0.0982735987 |
| parent bz cation **9**$^+$ ($C_i$ symmetry)<br><br>NUCLEAR ENERGY = 4453.4040361728<br>ELECTRONIC ENERGY = -7572.9367436295<br>TOTAL ENERGY = -3119.5327074567 | | | |
| C | 6.0 | 1.3684154088 | -0.0476401538 | -0.3075267797 |
| C | 6.0 | 0.6719706164 | -1.2351265532 | 0.0362916855 |
| C | 6.0 | -0.7106082334 | -1.1602596723 | 0.3437534780 |
| H | 1.0 | 2.4255811866 | -0.1079850879 | -0.5426580339 |
| H | 1.0 | -1.2430353335 | -2.0673196567 | 0.6092094760 |
| C | 6.0 | 1.9566920309 | -3.5240339680 | 0.0804088075 |
| C | 6.0 | 1.3469422655 | -2.4605675242 | 0.0652812855 |
| C | 6.0 | 2.0481734630 | -5.9532354195 | 0.3775298940 |
| C | 6.0 | 2.7442240420 | -7.1653999895 | 0.3885367739 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 4.1156098471 | -7.2774125660 | 0.1117792848 |
| C | 6.0 | 4.7857179551 | -6.0281574579 | -0.1651371103 |
| C | 6.0 | 4.0719825754 | -4.7736293287 | -0.1829205853 |
| C | 6.0 | 2.6608546393 | -4.7271883844 | 0.0910352894 |
| H | 1.0 | 0.9896804445 | -5.9574432523 | 0.6163027042 |
| H | 1.0 | 2.1940036880 | -8.0531782897 | 0.6709004094 |
| N | 7.0 | 6.0822793872 | -5.8910599960 | -0.4408065421 |
| N | 7.0 | 4.8382780780 | -3.7225722820 | -0.4655740375 |
| S | 16.0 | 6.3494557292 | -4.3009848709 | -0.6877611809 |
| S | 16.0 | 6.5190572781 | -8.6152888352 | 0.4990612243 |
| C | 6.0 | 6.4909178591 | -10.3205442685 | 0.4530216306 |
| C | 6.0 | 4.8060795547 | -8.5393621037 | 0.1332665243 |
| C | 6.0 | 5.2586706594 | -10.8457505933 | 0.1255964783 |
| C | 6.0 | 4.2829595668 | -9.8291037806 | -0.0623978898 |
| C | 6.0 | 4.9941669513 | -12.3139272923 | -0.0238395807 |
| C | 6.0 | 2.8863361061 | -10.1578739527 | -0.4992567930 |
| H | 1.0 | 7.3986619638 | -10.8757694518 | 0.6546191241 |
| H | 1.0 | 5.8792353524 | -12.8996437732 | 0.2333872863 |
| H | 1.0 | 4.1747925724 | -12.6427943825 | 0.6238221047 |
| H | 1.0 | 4.7183533909 | -12.5680029745 | -1.0538814212 |
| H | 1.0 | 2.8831472605 | -11.0763463936 | -1.0916582169 |
| H | 1.0 | 2.4487046732 | -9.3661460300 | -1.1114512064 |
| H | 1.0 | 2.2201649814 | -10.3332970417 | 0.3555071250 |

parent bz anion $\mathbf{9}^{-}$ ($C_i$ symmetry)

NUCLEAR ENERGY = 4437.7645186617
ELECTRONIC ENERGY = -7557.5935407721
TOTAL ENERGY = -3119.8290221104

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.3445100980 | -0.0487893300 | -0.3725861540 |
| C | 6.0 | 0.6941308989 | -1.2396846257 | 0.0353845047 |
| C | 6.0 | -0.6703687128 | -1.1537787966 | 0.4072214867 |
| H | 1.0 | 2.3903797242 | -0.1003278376 | -0.6591971254 |
| H | 1.0 | -1.1836465110 | -2.0567012088 | 0.7242008353 |
| C | 6.0 | 2.0111511088 | -3.5156592309 | 0.0872810822 |
| C | 6.0 | 1.3863327670 | -2.4619708151 | 0.0675342381 |
| C | 6.0 | 2.1119375557 | -5.9334351392 | 0.5152116400 |
| C | 6.0 | 2.8093006704 | -7.1452032279 | 0.5498091101 |
| C | 6.0 | 4.1528158033 | -7.2795267904 | 0.1801174332 |
| C | 6.0 | 4.8144279469 | -6.0697226605 | -0.2084183333 |
| C | 6.0 | 4.1009368213 | -4.8014516119 | -0.2461953889 |
| C | 6.0 | 2.7102872961 | -4.7280649496 | 0.1175060314 |
| H | 1.0 | 1.0707538202 | -5.9142656518 | 0.8217259964 |
| H | 1.0 | 2.2845486155 | -8.0224823901 | 0.9140301377 |
| N | 7.0 | 6.0974935424 | -5.9650900947 | -0.5675050618 |
| N | 7.0 | 4.8502264140 | -3.7712694133 | -0.6334126879 |
| S | 16.0 | 6.3563607245 | -4.3755937199 | -0.9207442691 |
| S | 16.0 | 6.4929265611 | -8.7006132409 | 0.7449670885 |
| C | 6.0 | 6.4568190465 | -10.4163459390 | 0.6269671521 |
| C | 6.0 | 4.8299388748 | -8.5704079129 | 0.2146145305 |
| C | 6.0 | 5.2522425408 | -10.8843618262 | 0.1761626361 |
| C | 6.0 | 4.3143189917 | -9.8269528768 | -0.0701207847 |
| C | 6.0 | 4.9521039909 | -12.3364864930 | -0.0549869642 |
| C | 6.0 | 2.9520370312 | -10.0903131816 | -0.6454841191 |
| H | 1.0 | 7.3409148330 | -10.9957092356 | 0.8611228437 |
| H | 1.0 | 5.8082068902 | -12.9620467237 | 0.2131407248 |
| H | 1.0 | 4.0937958590 | -12.6730757836 | 0.5392465021 |
| H | 1.0 | 4.7096624371 | -12.5396126956 | -1.1058065765 |

| | |
|---|---|
| H 1.0 3.0008037151 -10.8707959239 -1.4135100107<br>H 1.0 2.5355782597 -9.1912053307 -1.1051058682<br>H 1.0 2.2350267198 -10.4368786380 0.1110712288 | |
| cbz **2** ($C_i$ symmetry)<br><br>NUCLEAR ENERGY = 10629.0845827841<br>ELECTRONIC ENERGY = -15129.4170943155<br>TOTAL ENERGY = -4500.3325115314<br><br>C 6.0 -3.9014881553 0.1379792219 -0.0223047453<br>C 6.0 -3.1801758565 1.3214779018 -0.0229774077<br>C 6.0 -2.5549527222 2.3842341656 -0.0085336691<br>C 6.0 -1.8691428285 3.5843857269 0.0243895744<br>C 6.0 -0.4899173360 3.5503991612 0.0102409551<br>C 6.0 -0.7452203142 -3.5091239436 0.0181586564<br>C 6.0 -2.1235438317 -3.4453493105 0.0330065771<br>C 6.0 -2.7174103096 -2.1971986313 0.0001481775<br>C 6.0 -3.2620421769 -1.0914045934 -0.0180969433<br>C 6.0 -2.6021153907 4.8670817080 0.0728159610<br>C 6.0 -3.9846767431 4.9099934190 -0.1647870897<br>C 6.0 -4.6692594623 6.1187624877 -0.1240450314<br>C 6.0 -3.9906804949 7.3043163224 0.1583610157<br>C 6.0 -2.6182061150 7.2698520674 0.4045277603<br>C 6.0 -1.9292241586 6.0636657705 0.3635240278<br>C 6.0 -2.9495406780 -4.6697594329 0.0790984644<br>C 6.0 -2.3616741851 -5.9177486922 0.3378527000<br>C 6.0 -3.1375354613 -7.0699613130 0.3747258183<br>C 6.0 -4.5132717181 -6.9975815700 0.1557128718<br>C 6.0 -5.1068653993 -5.7602768878 -0.0936704501<br>C 6.0 -4.3362360213 -4.6042766967 -0.1296991207<br>H 1.0 -4.5132827117 3.9880036388 -0.3872018528<br>H 1.0 -5.7383611019 6.1367130369 -0.3162146416<br>H 1.0 -4.5281483980 8.2476268961 0.1902757558<br>H 1.0 -2.0827593978 8.1862911068 0.6356439963<br>H 1.0 -1.2942964987 -5.9720656709 0.5291584981<br>H 1.0 -2.6678442919 -8.0274867801 0.5814552756<br>H 1.0 -5.1189784580 -7.8988752696 0.1840715340<br>H 1.0 -4.8059494981 -3.6445443050 -0.3223952171<br>H 1.0 -0.8650197595 6.0351077734 0.5763911462<br>H 1.0 -6.1775614419 -5.6932622166 -0.2629161181<br>C 6.0 -6.5356431840 0.2111927812 -0.0071137565<br>C 6.0 -5.3162267249 0.1826450621 -0.0126180703<br>C 6.0 -8.6452560080 1.4584670602 0.0273189834<br>C 6.0 -10.0559784858 1.5180203400 0.0600135025<br>C 6.0 -10.8718823628 0.3962335675 0.0553888510<br>C 6.0 -10.1838900693 -0.8660279563 0.0420230095<br>C 6.0 -8.7371950925 -0.9361966884 0.0164189544<br>C 6.0 -7.9434209680 0.2614155194 0.0072032501<br>H 1.0 -8.0844882840 2.3874804826 0.0375714655<br>H 1.0 -10.5185866110 2.4966282348 0.1246631885<br>N 7.0 -10.7657520330 -2.0683487305 0.0427389984<br>N 7.0 -8.2603210369 -2.1813535704 0.0006824136<br>S 16.0 -9.5617159668 -3.1688268240 0.0197723388<br>S 16.0 -13.2856451492 -0.5936960613 1.0403003597<br>C 6.0 -14.7319696972 0.2266416122 0.6190827868<br>C 6.0 -12.3269550308 0.4986116616 0.0742189908<br>C 6.0 -14.5199880600 1.2692042723 -0.2439424618<br>C 6.0 -13.1315406147 1.4321980940 -0.5624044862<br>C 6.0 -15.6135105085 2.1303726334 -0.8033395238<br>C 6.0 -12.6592410903 2.4731427532 -1.5354068123 | |

| | | | | | |
|---|---|---|---|---|---|
| H | 1.0 | -15.6798995250 | -0.1147015178 | 1.0148117251 | |
| H | 1.0 | -16.5865572496 | 1.8407526908 | -0.3990189009 | |
| H | 1.0 | -15.4550077619 | 3.1890524890 | -0.5679988894 | |
| H | 1.0 | -15.6718464151 | 2.0491304783 | -1.8954160655 | |
| H | 1.0 | -13.3488055784 | 2.5467743043 | -2.3826881653 | |
| H | 1.0 | -11.6682933499 | 2.2402579665 | -1.9306690987 | |
| H | 1.0 | -12.6117013158 | 3.4706738584 | -1.0797961280 | |

cbz cation $\mathbf{2}^{+}$ ($C_i$ symmetry)

NUCLEAR ENERGY = 10643.6116516403
ELECTRONIC ENERGY = -15143.7302027466
TOTAL ENERGY = -4500.1185511063

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.8929772370 | 0.1489127445 | -0.0205329789 |
| C | 6.0 | -3.1675448068 | 1.3367383831 | -0.0265682631 |
| C | 6.0 | -2.5458827129 | 2.3972265240 | -0.0128004502 |
| C | 6.0 | -1.8566912341 | 3.6062759135 | 0.0214956904 |
| C | 6.0 | -0.4853441715 | 3.5562401534 | 0.0060868872 |
| C | 6.0 | -0.7532469556 | -3.5114809227 | 0.0248390606 |
| C | 6.0 | -2.1239101404 | -3.4550204906 | 0.0450495499 |
| C | 6.0 | -2.7143651064 | -2.1927749527 | 0.0124487243 |
| C | 6.0 | -3.2501797902 | -1.0879614121 | -0.0080717535 |
| C | 6.0 | -2.5868242884 | 4.8864147139 | 0.0728861452 |
| C | 6.0 | -3.9640361120 | 4.9335898751 | -0.1952157185 |
| C | 6.0 | -4.6463516548 | 6.1431804371 | -0.1523686116 |
| C | 6.0 | -3.9701968561 | 7.3215121328 | 0.1641938955 |
| C | 6.0 | -2.6031988322 | 7.2820626244 | 0.4417195090 |
| C | 6.0 | -1.9157869949 | 6.0763709422 | 0.3969910262 |
| C | 6.0 | -2.9548027254 | -4.6698863225 | 0.0944683870 |
| C | 6.0 | -2.3689879713 | -5.9230872535 | 0.3396920261 |
| C | 6.0 | -3.1508228265 | -7.0693901411 | 0.3767119491 |
| C | 6.0 | -4.5289182749 | -6.9854259351 | 0.1707451293 |
| C | 6.0 | -5.1197860427 | -5.7440542839 | -0.0643214713 |
| C | 6.0 | -4.3439165123 | -4.5922548230 | -0.0994883456 |
| H | 1.0 | -4.4897930673 | 4.0174974225 | -0.4461255694 |
| H | 1.0 | -5.7102019844 | 6.1687219754 | -0.3689519783 |
| H | 1.0 | -4.5059672643 | 8.2653028624 | 0.1989991254 |
| H | 1.0 | -2.0735185204 | 8.1938599920 | 0.7008841256 |
| H | 1.0 | -1.3005613136 | -5.9860150193 | 0.5214018504 |
| H | 1.0 | -2.6870610328 | -8.0313570099 | 0.5730978083 |
| H | 1.0 | -5.1387457844 | -7.8834613558 | 0.1988478626 |
| H | 1.0 | -4.8110659698 | -3.6293198034 | -0.2814502289 |
| H | 1.0 | -0.8573593181 | 6.0432491174 | 0.6360607024 |
| H | 1.0 | -6.1914550444 | -5.6723424242 | -0.2224890642 |
| C | 6.0 | -6.5173369629 | 0.2113188741 | -0.0154824170 |
| C | 6.0 | -5.2917300282 | 0.1899784867 | -0.0166262568 |
| C | 6.0 | -8.6278396965 | 1.4442577770 | -0.0604572422 |
| C | 6.0 | -10.0284322343 | 1.4974102093 | -0.0505396095 |
| C | 6.0 | -10.8442385209 | 0.3633417312 | 0.0021303110 |
| C | 6.0 | -10.1416823215 | -0.8943214688 | 0.0726248592 |
| C | 6.0 | -8.6978345102 | -0.9581357024 | 0.0582262800 |
| C | 6.0 | -7.9130116057 | 0.2446300634 | -0.0118641923 |
| H | 1.0 | -8.0710806631 | 2.3752634960 | -0.0892159792 |
| H | 1.0 | -10.4931553763 | 2.4753216304 | -0.0387490711 |
| N | 7.0 | -10.7148351139 | -2.0968070289 | 0.1387396850 |
| N | 7.0 | -8.2136178301 | -2.1972745921 | 0.1163121266 |
| S | 16.0 | -9.5089358891 | -3.1921616338 | 0.1870539481 |
| S | 16.0 | -13.2507224427 | -0.7205248918 | 0.8792004514 |
| C | 6.0 | -14.6871700563 | 0.1328425628 | 0.5192406536 |
| C | 6.0 | -12.2867430489 | 0.4523218958 | 0.0095487716 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -14.4808938294 | 1.2409810609 | -0.2685375673 |
| C | 6.0 | -13.0992936366 | 1.4325917944 | -0.5673632324 |
| C | 6.0 | -15.5828905983 | 2.1303673369 | -0.7622178811 |
| C | 6.0 | -12.6365062938 | 2.5348211078 | -1.4742443810 |
| H | 1.0 | -15.6354374186 | -0.2317286861 | 0.8941383348 |
| H | 1.0 | -16.5482962821 | 1.8190812186 | -0.3570836883 |
| H | 1.0 | -15.4194074452 | 3.1741582506 | -0.4732430878 |
| H | 1.0 | -15.6599738790 | 2.1040239894 | -1.8554784491 |
| H | 1.0 | -13.3830203182 | 2.7246060555 | -2.2508789500 |
| H | 1.0 | -11.6952371027 | 2.2893997852 | -1.9709387955 |
| H | 1.0 | -12.4967987573 | 3.4804948893 | -0.9345199115 |

cbz anion **2**$^{-}$ ($C_i$ symmetry)

NUCLEAR ENERGY = 10619.2471287644
ELECTRONIC ENERGY = -15119.6745032382
TOTAL ENERGY = -4500.4273744738

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.9378918597 | 0.1481106387 | -0.0161481803 |
| C | 6.0 | -3.2092730525 | 1.3389830924 | -0.0152289233 |
| C | 6.0 | -2.5706266637 | 2.3895113060 | -0.0034253997 |
| C | 6.0 | -1.8638139972 | 3.5907013647 | 0.0275468098 |
| C | 6.0 | -0.4934187251 | 3.5569739622 | 0.0173939376 |
| C | 6.0 | -0.7472658054 | -3.5093566226 | 0.0097800916 |
| C | 6.0 | -2.1159446313 | -3.4311337966 | 0.0289033334 |
| C | 6.0 | -2.7199849101 | -2.1763319546 | 0.0008926695 |
| C | 6.0 | -3.2806203484 | -1.0822639902 | -0.0132517720 |
| C | 6.0 | -2.5965131344 | 4.8739838095 | 0.0701906916 |
| C | 6.0 | -3.9803456396 | 4.9162448502 | -0.1631505649 |
| C | 6.0 | -4.6678992917 | 6.1242153265 | -0.1265299508 |
| C | 6.0 | -3.9933179894 | 7.3138839050 | 0.1471606393 |
| C | 6.0 | -2.6194941987 | 7.2810828251 | 0.3889985407 |
| C | 6.0 | -1.9284314402 | 6.0760536273 | 0.3528018453 |
| C | 6.0 | -2.9558125167 | -4.6473058125 | 0.0793797134 |
| C | 6.0 | -2.3801107881 | -5.9108427384 | 0.2872223753 |
| C | 6.0 | -3.1708439508 | -7.0527198235 | 0.3295826408 |
| C | 6.0 | -4.5538779618 | -6.9581624869 | 0.1697503333 |
| C | 6.0 | -5.1360030970 | -5.7062835119 | -0.0271522727 |
| C | 6.0 | -4.3492139454 | -4.5607485379 | -0.0709552871 |
| H | 1.0 | -4.5066328729 | 3.9907201099 | -0.3765937252 |
| H | 1.0 | -5.7384237345 | 6.1363601588 | -0.3140422674 |
| H | 1.0 | -4.5330048938 | 8.2564084864 | 0.1769449516 |
| H | 1.0 | -2.0837175459 | 8.1994143866 | 0.6147450948 |
| H | 1.0 | -1.3065801006 | -5.9832497465 | 0.4334330883 |
| H | 1.0 | -2.7057730786 | -8.0211103218 | 0.4951577637 |
| H | 1.0 | -5.1718579311 | -7.8513582667 | 0.2042742260 |
| H | 1.0 | -4.8115598278 | -3.5899094401 | -0.2213122026 |
| H | 1.0 | -0.8635035212 | 6.0495163207 | 0.5633254800 |
| H | 1.0 | -6.2120624191 | -5.6164774086 | -0.1472729109 |
| C | 6.0 | -6.5661088459 | 0.1977389777 | 0.0009302283 |
| C | 6.0 | -5.3405051952 | 0.1824696910 | -0.0057212483 |
| C | 6.0 | -8.6775047086 | 1.4457445968 | 0.0512062855 |
| C | 6.0 | -10.0824558569 | 1.4940220718 | 0.0751570715 |
| C | 6.0 | -10.8998462879 | 0.3676394340 | 0.0472305447 |
| C | 6.0 | -10.2119890756 | -0.8912693849 | 0.0273217429 |
| C | 6.0 | -8.7606575365 | -0.9556317289 | 0.0087431874 |
| C | 6.0 | -7.9637474880 | 0.2457010188 | 0.0151551318 |
| H | 1.0 | -8.1195031349 | 2.3758929062 | 0.0793990842 |
| H | 1.0 | -10.5516725612 | 2.4697792036 | 0.1491950861 |
| N | 7.0 | -10.7902218440 | -2.0957700711 | 0.0202777910 |

| | | | | |
|---|---|---|---|---|
| N | 7.0 | -8.2789968501 | -2.1964371384 | -0.0124628657 |
| S | 16.0 | -9.5762732261 | -3.1963666376 | -0.0041978320 |
| S | 16.0 | -13.3276344210 | -0.6249907857 | 1.0074778864 |
| C | 6.0 | -14.7723216161 | 0.2080368245 | 0.5925847797 |
| C | 6.0 | -12.3560586065 | 0.4729668581 | 0.0567260927 |
| C | 6.0 | -14.5478578830 | 1.2604424191 | -0.2533493577 |
| C | 6.0 | -13.1566416335 | 1.4158137816 | -0.5694449135 |
| C | 6.0 | -15.6328138245 | 2.1399267497 | -0.8020491661 |
| C | 6.0 | -12.6725601995 | 2.4613426414 | -1.5324597215 |
| H | 1.0 | -15.7250573508 | -0.1375095547 | 0.9727597723 |
| H | 1.0 | -16.6099209058 | 1.8514655321 | -0.4050782176 |
| H | 1.0 | -15.4666230873 | 3.1937590298 | -0.5485549048 |
| H | 1.0 | -15.6893784426 | 2.0803851828 | -1.8960586225 |
| H | 1.0 | -13.3592172890 | 2.5507501578 | -2.3814207723 |
| H | 1.0 | -11.6836784497 | 2.2163621299 | -1.9257968648 |
| H | 1.0 | -12.6091186438 | 3.4560073248 | -1.0714814331 |