

Preparation, X-ray structure and properties of a hexabrominated, symmetric indole trimer and its TCNQ adduct: a new route to functional molecular systems

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Reaction of indole with Br₂ led to isolation of an indole trimer **2**, formed by linking the 2- and 3-positions of each indole to form a central aromatic ring, and brominated at the 5- and 6-positions of each indole. The X-ray structure of [2]·acetone·2DMF showed π -stacking of the planar aromatic molecules with two different overlap modes with interplanar distances of 3.287 Å and 3.378 Å. Cyclic voltammetry showed one reversible oxidation for **2** and phosphorescence from frozen ethanol solution was observed. The X-ray structure of the adduct [2][TCNQ]₂·4DMSO was determined and showed a mixed stack arrangement where **2** alternates with two adjacent TCNQ molecules.

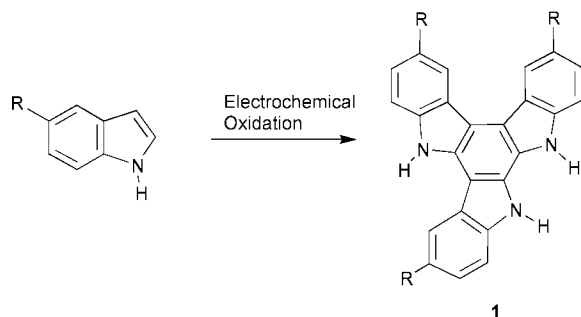
Introduction

The study of electrochemical polymerisation of indole and substituted analogues has been pursued for a number of years in the quest for new conducting polymers and functional systems.^{1,2} It has been shown that the initial product of this process comprises an asymmetric indole trimer **1** (Scheme 1) formed by fusing the edges of three indole molecules to give an extended π -system. Detailed NMR studies³ have confirmed the asymmetric structure of the electrochemically generated trimer and, considered alongside electrochemical parameters and mass spectroscopic evidence,¹ indicate trimers or linked trimers to be the dominant component of the electrooxidation product. Such asymmetric trimers and the symmetric analogues have been reported previously *via* synthetic organic routes involving multistep reactions, chromatographic purification and a low overall yield.^{4,5} A partial X-ray structure was also reported for **1** in the oxidised form, prepared by an electrochemical route, but this showed little more than a probable space group and a trimer stacking distance.⁶ The structure of an asymmetric trimer has been reported with acyl functionality at one of the N-positions⁷ but no further investigation of the properties of this species appears to have been undertaken.

The attractive properties of these molecules in the field of functional molecular materials include reversible one-electron oxidation, high quantum yield fluorescence, π -stacking in the

solid state and ease of further derivatisation around the periphery. Thus, these compounds possess analogous properties to other functional molecules widely used in materials synthesis. The redox properties and π -stacking capability are comparable with those of tetrathiafulvalene-derived species (TTF) capable of forming molecular superconductors⁸ and parallels can also be drawn with derivatised phthalocyanines capable of self assembly into conducting solids and molecular wires.⁹ The fluorescence properties and ease of derivatisation suggest potential in light emitting materials and optical as well as electrochemical sensors. In order to fully explore indole trimers as a new family of functional molecules, we have undertaken the chemical oxidation of indole in order to establish a straightforward route to the trimer and produce quantities of compound suitable for materials applications.

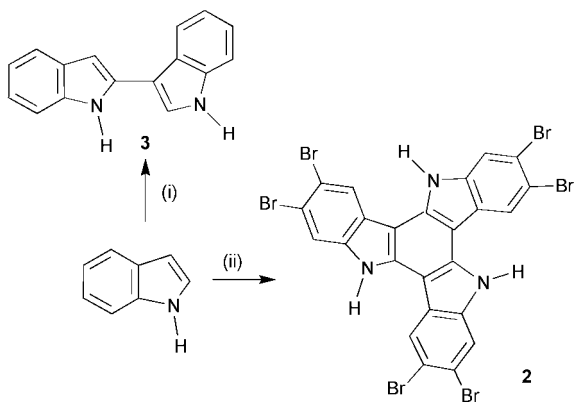
We have explored the reaction between indole or 5-substituted indoles and oxidising reagents such as FeCl₃, I₂ and Br₂. Although some previous studies have involved chemical oxidation of indoles, these have paid no attention to the molecular characterisation of the oxidised product and focused only on the morphology and conductivity of resultant films.¹⁰ This paper reports the reaction between indole and Br₂ in different ratios as these reactions have led to well characterised, indole trimer and dimer products in a satisfactory yield by a one-pot reaction followed by recrystallisation. Reactions with other oxidising agents will be reported later.



Scheme 1 Electrochemical trimerisation of indole.

Results and discussion

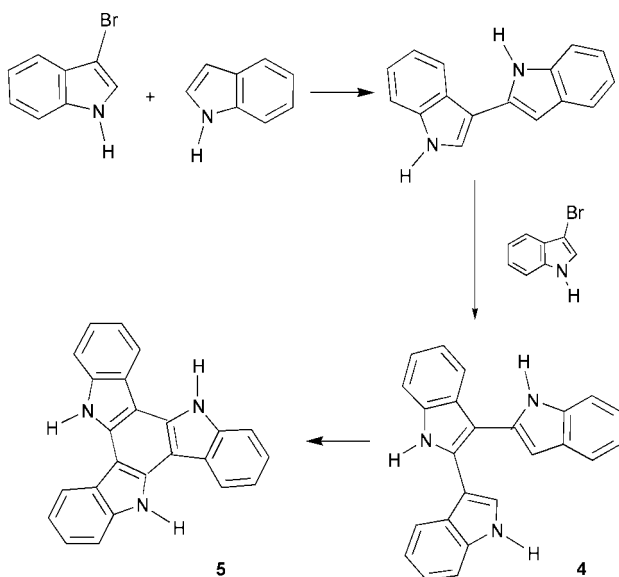
The reaction of indole with three equivalents of Br₂ was undertaken in CH₃CN and led to isolation of a dark precipitate. This was shown by NMR to consist in large part of the symmetric, brominated trimer **2** (Scheme 2) in 59% yield and purity sufficient for further synthesis in some cases. Upon recrystallisation a high purity sample of **2** was obtained in an overall yield of 18%. In addition to NMR, mass spectrometry and elemental analysis were consistent with the structure of a symmetric indole trimer brominated six times at the 5- and 6-positions of indole.



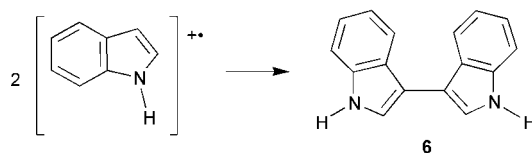
Scheme 2 Reactions of indole with Br₂ in CH₃CN (i) 0.5 equivalents (ii) 3 equivalents.

The reaction of indole with 0.5 equivalents of Br₂ in CH₃CN led to the isolation of a pale solid in 80% yield which was shown by NMR to be the asymmetric indole dimer **3** (Scheme 2). This was also confirmed by elemental analysis and mass spectrometric results. The high yield isolation of 2,3-dimer indicates a mechanism which is likely to involve bromination of indole at the 3-position, as this is known to be able to react with another molecule of indole to cause coupling in a 2,3-manner.⁵ Reaction of this species with a further equivalent of 3-bromoindole has been shown⁵ to cause coupling to give **4** which can be cyclised under acidic conditions to the symmetric trimer **5** (Scheme 3). Clearly, cyclisation of **4** can lead only to symmetric trimer and compound **1** (R = H) cannot be achieved by this route. In contrast to literature studies however, our procedure involves sequential bromination and coupling steps *in situ* and avoids any requirement to isolate and purify intermediates. The symmetric nature of **2** is a consequence of the asymmetric dimer **3** and gives indirect support to the mechanism proposed for the electrochemical formation of asymmetric trimer **1**.¹ This mechanism involves initial coupling of two radical cations of indole *via* the 3-position as this is calculated to be the position of highest electron density (Scheme 4).¹¹ Clearly, the symmetric dimer intermediate **6** can lead only to asymmetric indole trimer in contrast to the dimer **3** obtained *via* the bromination reaction.

The addition of one equivalent of Br₂ to indole was also carried out in the anticipation of causing two sequential oxidations of each indole leading to unsubstituted trimer plus



Scheme 3 Reaction of 3-bromoindole and indole under acidic conditions.



Scheme 4 Proposed initial mechanistic step of electrochemical oxidation of indole.

2HBr. This reaction however, also leads only to the isolation of the 2,3-dimer with slightly reduced purity. It is unclear at present why this reaction does not proceed beyond formation of the 2,3-dimer.

There are several advantages to our synthetic method. Firstly, a one-pot reaction is used, involving only cheap, commercially available reagents, which simplifies the procedure and allows an easy increase in scale. Secondly the hexabromination allows the trimer to be readily isolated due to its lower solubility, avoiding lengthy chromatographic procedures. In the case of **3**, the product also precipitates and is isolated as an HBr adduct with low solubility. The bromination also gives a product ideal for further substitutions at Br to exploit the trimer in materials applications without the need to use expensive substituted indole precursors. Furthermore, the presence of large halogen atoms around the periphery of the molecule is likely to increase the opportunity for intermolecular interactions in salts of the compound required to achieve cooperative electronic properties such as high conductivity or magnetism.

Slow diffusion of acetone into a DMF solution of **2** led to colourless crystals of [2]·acetone·2DMF which were characterised by X-ray crystallography (Fig. 1). Molecules of **2** are found to adopt a planar configuration with a mean deviation from the plane of 0.0565 Å. Within the trimer molecule, the central aromatic ring shows no significant differences between C–C bonds. Likewise, within the five and six-membered rings of the indole moieties, bond lengths appear typical for this type of system and the trimer unit can be considered to be fully delocalised. The C–Br bond lengths show no significant differences within the errors of the data and average to a value of 1.895 Å. This is typical of Br bound to an aromatic system and is comparable to values for 1,2,4,5-tetrabromobenzene.¹²

The trimers form a stack along the (100)-axis (Fig. 2) with adjacent molecules related by a centre of inversion. Two different overlaps exist with one centred around a cell corner (Fig. 3) and an interplanar distance of 3.287 Å and the other centred around a cell edge (Fig. 4) with an interplanar distance of 3.378 Å. The stacks are separated by solvent molecules which show H-bonding to the NH groups of the trimer with

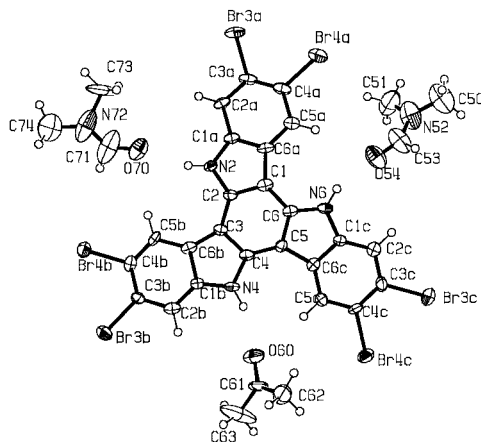


Fig. 1 X-Ray structure of [2]·acetone·2DMF showing atom labelling scheme.

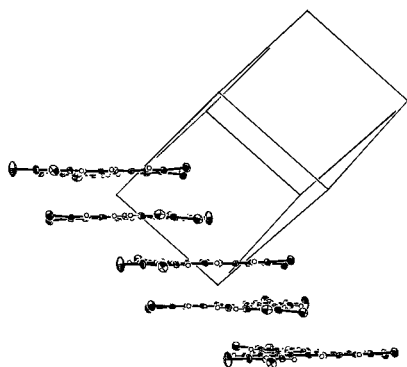


Fig. 2 Stacks of **2** along the (100) axis with solvent removed for clarity.

O \cdots N distances of 2.887 and 2.804 Å and O–H–N angles of 162.29° and 158.74° for the DMF molecules and an O \cdots N distance of 2.880 Å and O–H–N angle of 159.43° for the acetone molecule. The stacks are linked into a three dimensional network *via* intermolecular Br \cdots Br contacts of 3.414 and 3.597 Å which are within the sum of the van der Waals radii of two Br atoms (3.8 Å). The π -stacking interaction and the short Br \cdots Br contacts suggest that oxidised or partially oxidised salts of the trimer will be capable of displaying cooperative electronic behaviour analogous to the conducting and magnetic properties of salts such as the TTF or phthalocyanine classes.

An important strategy for forming conducting molecular crystals from electron-donor organic molecules such as TTF involves formation of charge-transfer salts with electron acceptors such as tetracyano-*p*-quinodimethane (TCNQ) and its analogues.^{13,14} To assess the potential of **2** in this respect we studied its reaction with TCNQ. Single crystals of [2][TCNQ]₂·4DMSO were grown by mixing DMSO solutions of the components and standing over several days. The structure shows a mixed stack arrangement comprising indole trimer molecules alternating with two side-by-side TCNQ molecules (Fig. 5). Such an unusual packing motif is presumably adopted due to the size difference between the TCNQ molecules and **2** such that the adjacent pair of TCNQ molecules occupies a comparable space to the single indole trimer and efficient packing into the stack can occur. The crystals contain four molecules of DMSO per formula unit however, due to the poor quality of the data, only three of these could be satisfactorily positioned within the cell. Again H-bonding is observed between the indole NH and DMSO with an O \cdots N distance of 2.850 Å and angle of 162.6°. Within the limits of the data obtained, the geometric parameters in the trimer are comparable to those shown in the structure discussed above and those of the TCNQ molecules are comparable to literature analogues.¹⁵ The molecules of **2** again show an approximately planar arrangement with a mean deviation of 0.0545 Å as do the two inequivalent TCNQ molecules with mean deviations of 0.0585 Å and 0.1391 Å. The separation between the plane of the trimer molecule and a point centred between the two side-by-side TCNQ molecules was found to be 3.3172 Å and the mean plane of the TCNQ molecules was found to make an angle of 5.2° with the plane of the trimer molecule. No interstack Br \cdots Br contacts were found to be shorter than 3.814 Å.

Cyclic voltammetry was carried out on the brominated trimer **2** by drop coating a DMF solution of the trimer onto a platinum electrode, allowing the solution to dry overnight and running the voltammogram using an acetonitrile solution with 0.1 M LiClO₄ as electrolyte. This showed a single oxidation process at +0.67 V against Ag/Ag⁺ (0.01 M) and a broad return peak, observed around 0.5 V (Fig. 6). Thus, **2** shows a chemically-reversible redox process, analogous to that observed for **1**, indicating stability of **2** in the oxidised form. The difference in the peak shapes of the oxidised and reduced

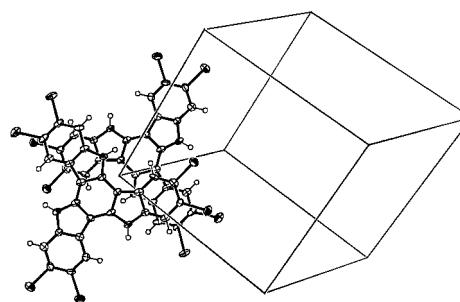


Fig. 3 Overlap of two molecules of **2** related by an inversion centre at the cell corner.

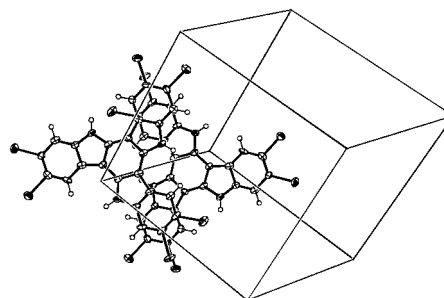


Fig. 4 Overlap of two molecules of **2** related by an inversion centre at the cell edge.

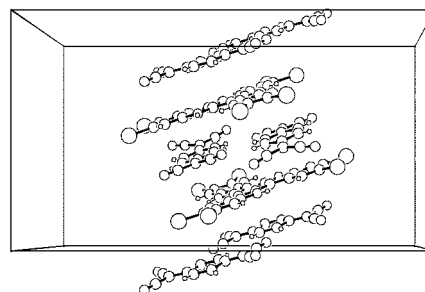


Fig. 5 Stacking in crystals of [2][TCNQ]₂·4DMSO with solvent removed for clarity viewed along the (001) axis.

forms has previously been observed for other indole trimers.^{1,2} This has been attributed to the difference in structure between the compact lyophobic film when reduced and the more open, lyophilic film when oxidised. The standard redox potential of the film would be expected, as with other indoles, to lie between the trimer redox peaks at around 0.58 V. This value is comparable with the standard redox potential of the asymmetric 5-bromoindole trimer (**1**, R = Br), whose standard redox potential has been recorded at about 0.50 V.² It must be remembered that in this case, the trimer **1** (R = Br) has only three attached Br atoms at the periphery in contrast to **2** which

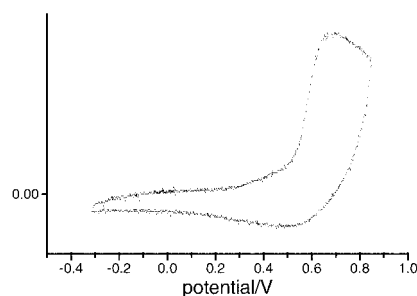


Fig. 6 Cyclic voltammogram of a drop coated film of **2** in CH₃CN–0.1 M LiClO₄. Potentials are reported with respect to the Ag/Ag⁺(0.01 M) reference electrode in background electrolyte. The sweep rate was 50 mV s⁻¹.

has six. This would be expected to increase the redox potential of **2** slightly due to the weakly electron-withdrawing nature of the bromines.² These results are therefore consistent with the one-electron redox behaviour typical of asymmetric indole trimer based species, indicating that both symmetric and asymmetric trimer units have similar redox potentials. The dimer **3** has shown electrochemical oxidation followed by reaction and a detailed study of the electrochemical and film forming properties of **3** will be reported elsewhere.

In order to achieve highly conducting charge-transfer salts, some degree of partial electron transfer must take place between donor and acceptor molecules. The capability for such a charge transfer can be estimated by consideration of the redox potentials of the two components.¹⁶ An accurate comparison can not be made in the case of **2** and TCNQ as the low solubility of **2** did not allow determination of the redox parameters under standard conditions. An estimate can be made however based on the data recorded for the drop coated film and suggests that little charge transfer would be expected in this system. This view is supported by IR data which shows a value of 2219 cm^{-1} for the CN stretch of the TCNQ in the crystals of $[2][\text{TCNQ}]_2 \cdot 4\text{DMSO}$. This compares closely with the value of 2220 cm^{-1} for neutral TCNQ and is well removed from the value of 2180 cm^{-1} typical for TCNQ^- . Clearly however, some driving force for the co-crystallisation of these components exists as the crystals formed from a solution in which **2** and TCNQ are both soluble. This suggests that crystallisation of **2** with substituted TCNQ analogues with greater electron accepting capability should be readily achieved and should yield conducting crystals. Such a strategy is well established in the field of conducting charge-transfer salts.^{13,14}

Electrical conductivity measurements were carried out by the 4-probe method at room temperature on a compressed pellet of **2** and a crystal of $[2][\text{TCNQ}]_2 \cdot 4\text{DMSO}$ and gave values of the order $10^{-7} \text{ S cm}^{-1}$ and $10^{-6} \text{ S cm}^{-1}$ respectively. The value for **2** is consistent with that expected for an undoped molecular π -stacked solid and the value for the TCNQ adduct is also expected to have a low value from the mixed-stack packing of the components and the lack of significant charge transfer between the molecules.

Indole-based species typically show high quantum yield fluorescence and this is typified by the dimer **3** which shows an emission maximum at 389 nm and corresponding absorption maximum at 309 nm (Fig. 7). This is compared with the parent indole molecule, which shows corresponding values of 334 nm and 280 nm and the shift to lower energy reflects the larger degree of delocalisation in the dimer molecule. The hexabrominated trimer molecule **2** shows no fluorescence and this can be attributed to the heavy atom effect arising from the presence of the six heavy bromine atoms. Recording of the emission spectrum in frozen ethanol however leads to the observation of peaks that can be assigned as arising from intersystem crossing to the T_1 triplet state (Fig. 8). Both the emission and the absorption peaks show at least two vibrational progressions as

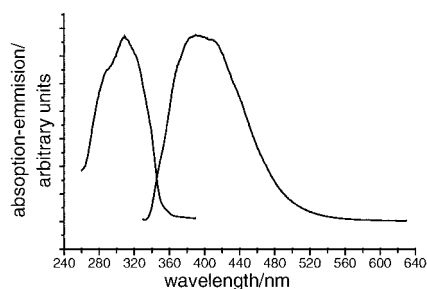


Fig. 7 Emission and corresponding excitation spectrum for **3** in CH_3CN . Spectra recorded at fixed excitation and emission wavelengths of 320 nm and 400 nm respectively.

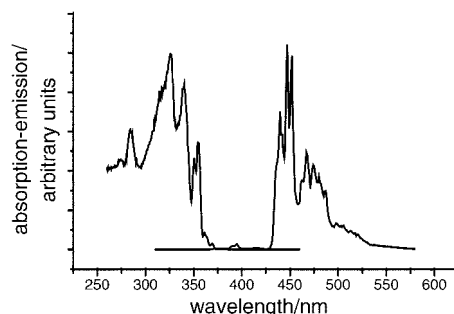


Fig. 8 Emission and corresponding excitation spectrum for **2** in ethanol. Spectra recorded at fixed excitation and emission wavelengths of 300 nm and 475 nm respectively.

would be anticipated in a multiply substituted aromatic molecule of this size.

Conclusion

We have prepared an electronically delocalised indole trimer by a straightforward route using cheap reagents in a one-pot reaction. The X-ray structure of the molecule illustrates its capability for π -stacking and the crystallisation of an adduct with TCNQ suggests a utility in conducting charge-transfer salts. In addition, the trimer shows a reversible one-electron oxidation, has Br and NH groups available for further derivatisation and shows phosphorescence in frozen DMSO. The combination of these properties indicates a wide-reaching potential for such a compound and its analogues to be applied to a range of functional molecular systems such as molecular and polymeric conductors, optical materials and sensors.

Experimental

Indole and Br_2 were purchased from Aldrich and used without further purification. Solvents used were HPLC grade and required no further drying or purification.

Preparation of **2**

Indole (2.72 g, 23.3 mmol) was stirred in acetonitrile (50 ml) and Br_2 (11.22 g, 70.1 mmol) in acetonitrile (15 ml) added over 5 min. The mixture was stirred overnight and the resulting dark green solid was filtered and washed with acetonitrile (600 ml) (crude yield = 3.75 g, 4.58 mmol, 59%). A portion of the solid (1.06 g) was recrystallised by addition of acetone (250 ml) to a DMSO (10 ml) solution of the product (overall yield = 0.324 g, 18 %). Calc for $\text{C}_{24}\text{H}_9\text{N}_3\text{Br}_6 \cdot \text{C}_3\text{H}_6\text{O}$, C, 36.9; H, 1.7; N, 4.8; found, C, 36.4; H, 2.0; N, 4.5%. $^1\text{H NMR}$ (DMSO): 12.11 (3H, s), 8.86 (3H, s), 7.85 (3H, s). IR (KBr disc)/ cm^{-1} : 3362, 1706, 1633, 1600, 1469, 1431, 1399, 1361, 1296, 1264, 1225, 1074, 1025, 949, 920, 866, 845, 701, 634, 529. UV/vis (DMSO): λ_{max} = 323 nm ($\epsilon = 16300 \text{ M}^{-1} \text{ cm}^{-1}$), 343 nm ($10600 \text{ M}^{-1} \text{ cm}^{-1}$), 357 nm ($6200 \text{ M}^{-1} \text{ cm}^{-1}$)

Preparation of $3 \cdot \text{HBr}_{1.33}$

Indole (0.477 g, 4.08 mmol) was stirred in acetonitrile (10 ml) and Br_2 (0.33 g, 2.06 mmol) in acetonitrile (5 ml) added over 5 min. The mixture was stirred overnight and the pale brown product was filtered and washed with acetone. Yield = 0.535 g, 3.15 mmol, 77%. Calc for $\text{C}_{16}\text{H}_{12}\text{N}_2 \cdot (\text{HBr})_{1.33}$, C, 56.5; H, 3.9; N, 8.2; found, C, 56.5; H, 3.6; N, 8.3%. $^1\text{H NMR}$ (DMSO): 11.41 (1H, s), 11.22 (1H, s), 7.99 (1H, d), 7.87 (1H, d), 7.48 (2H, multiplet), 7.35 (1H, d), 7.16 (2H, multiplet), 6.99 (2H, multiplet), 6.75 (1H, d). IR (KBr disc)/ cm^{-1} : 3100, 1622, 1576, 1496, 1436, 1370, 1306, 1252, 1230, 1014, 984, 874, 830,

750, 707, 644, 608, 586, 560, 506. UV/vis (DMSO): $\lambda_{\text{max}} = 318\text{nm}$ ($\epsilon = 8800\text{ M}^{-1}\text{ cm}^{-1}$)

Crystal data for $2 \cdot (\text{C}_3\text{H}_7\text{NO})_2(\text{C}_2\text{H}_6\text{O})^\dagger$

$\text{C}_{33}\text{H}_{29}\text{Br}_6\text{N}_5\text{O}_3$, triclinic, space group $P\bar{1}$, $a = 10.2450(16)\text{Å}$, $b = 12.6915(19)\text{Å}$, $c = 13.557(2)\text{Å}$, $\alpha = 80.371(3)^\circ$, $\beta = 87.000(3)^\circ$, $\gamma = 85.967(3)^\circ$, $V = 1732.2(5)\text{Å}^3$, $Z = 2$. Data were collected using a synchrotron radiation source with $\lambda = 0.68840\text{Å}$ at $T = 150(2)\text{K}$. 13879 reflections were collected of which 6668 were independent. Refinement converged to $R_1 = 0.0654$ ($I > 2\sigma I$), $wR_2 = 0.1581$ (all data), $\text{GOF} = 1.037$.

Crystal data for $[\text{2}][\text{TCNQ}]_2 \cdot 4\text{DMSO}^\dagger$

$\text{C}_{56}\text{H}_{41}\text{Br}_6\text{N}_{11}\text{O}_4\text{S}_4$, monoclinic, space group $P2_1/c$, $a = 14.455(3)\text{Å}$, $b = 25.371(5)\text{Å}$, $c = 16.719(3)\text{Å}$, $\beta = 93.24(3)^\circ$, $V = 6122(2)\text{Å}^3$, $Z = 4$, $\lambda = 1.54178\text{Å}$, $T = 220(2)\text{K}$. 8438 reflections were collected of which 6965 were independent. Refinement converged to $R_1 = 0.0868$ ($F > 4\sigma F$), $wR_2 = 0.2476$ (all data), $\text{GOF} = 0.955$.

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References

- 1 J. G. Mackintosh, C. R. Redpath, A. C. Jones, P. R. R. Langridge-Smith and A. R. Mount, *J. Electroanal. Chem.*, 1995, **388**, 179; J. G. Mackintosh and A. R. Mount, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1121.
- 2 P. Jennings, A. C. Jones, A. R. Mount and A. D. Thomson, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3791.
- 3 J. G. Mackintosh, A. R. Mount and D. Reed, *Magn. Reson. Chem.*, 1994, **32**, 559.
- 4 J. Bergman and N. Eklund, *Tetrahedron*, 1980, **36**, 1445.
- 5 V. Bocchi and G. Palla, *Tetrahedron*, 1986, **42**, 5019.
- 6 V. Bocchi, A. Colombo and W. Porzio, *Synth. Met.*, 1996, **80**, 309.
- 7 T. Kaneko, M. Matsuo and Y. Iitaki, *Chem. Pharm. Bull.*, 1981, **29**, 3499.
- 8 A. E. Underhill, *J. Mater. Chem.*, 1992, **2**, 1.
- 9 N. B. McKeown, *Phthalocyanine Materials*, Cambridge University Press, Cambridge, 1998.
- 10 D. Billaud, E. B. Maarouf and E. Hannecart, *Synth. Met.*, 1995, **69**, 571; D. Billaud, E. B. Maarouf and E. Hannecart, *Mater. Res. Bull.*, 1994, **29**, 1239.
- 11 L. J. Kettle, S. P. Bates and A. R. Mount, *Phys. Chem. Chem. Phys.*, 2000, **2**, 195.
- 12 G. Gafner and F. H. Herstein, *Acta Crystallogr.*, 1960, **13**, 706.
- 13 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916; R. C. Wheland, *J. Am. Chem. Soc.*, 1976, **98**, 3926.
- 14 N. Martin, J. L. Segura and C. Seoane, *J. Mater. Chem.*, 1997, **7**, 1661.
- 15 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Crystallogr., Sect. C*, 1965, **18**, 932.
- 16 G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141.

[†]CCDC reference number 1145/230. See <http://www.rsc.org/suppdata/jm/b0/b003631p/> for crystallographic files in .cif format.