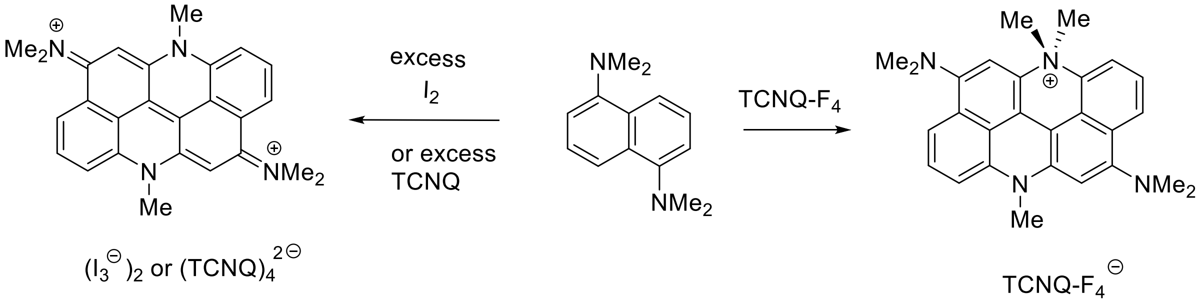
# One Step Conversion of 1,5-*bis*(Dimethylamino)naphthalene to Salts of “Back to Back” *bis*-Acridine Derivatives.

**Songjie Yang, Jonathan C. Bristow, Matthew A. Addicoat, John D. Wallis,***

**School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK.**

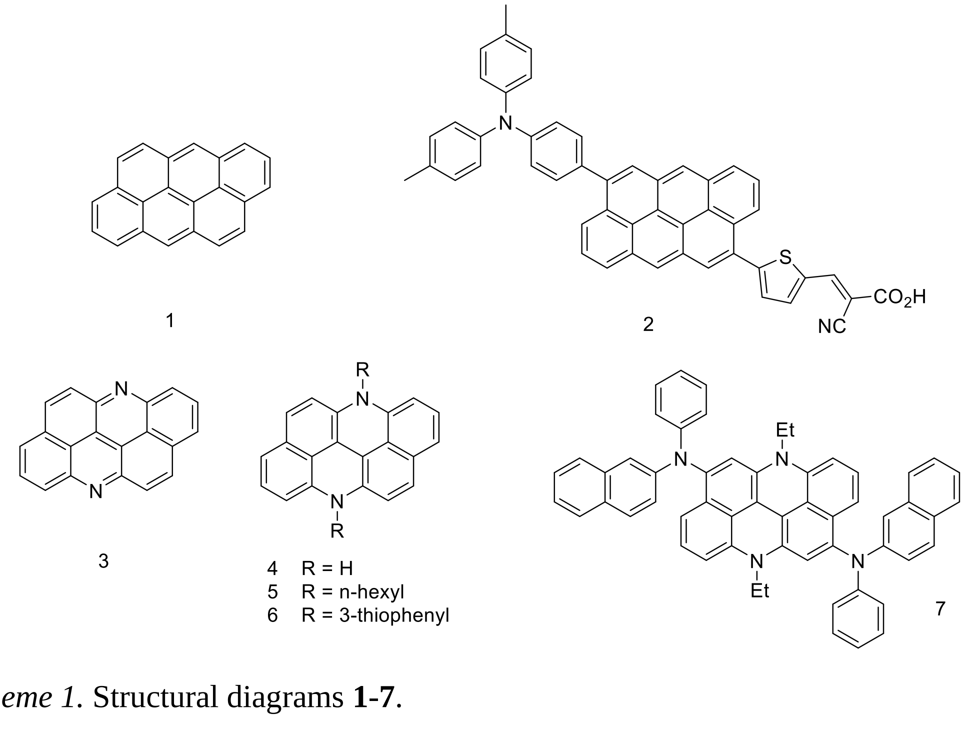
## Abstract.

Oxidation of 1,5-*bis*(dimethylamino)naphthalene with iodine leads directly to a bis(dimethyliminium) derivative of acridino[2,1,9,8-*klmna*]acridine, containing six fused six-membered rings, as a *bis* triiodide salt. The cation has a twisted structure due to the minimisation of *peri* interactions between each dimethyliminium group and a hydrogen atom. Use of TCNQ as oxidizing agent leads to the same dication as a *tetrakis*(TCNQ) salt, while use of TCNQ-F4 gave a related monocation which is dimethylated on a ring nitrogen atom.



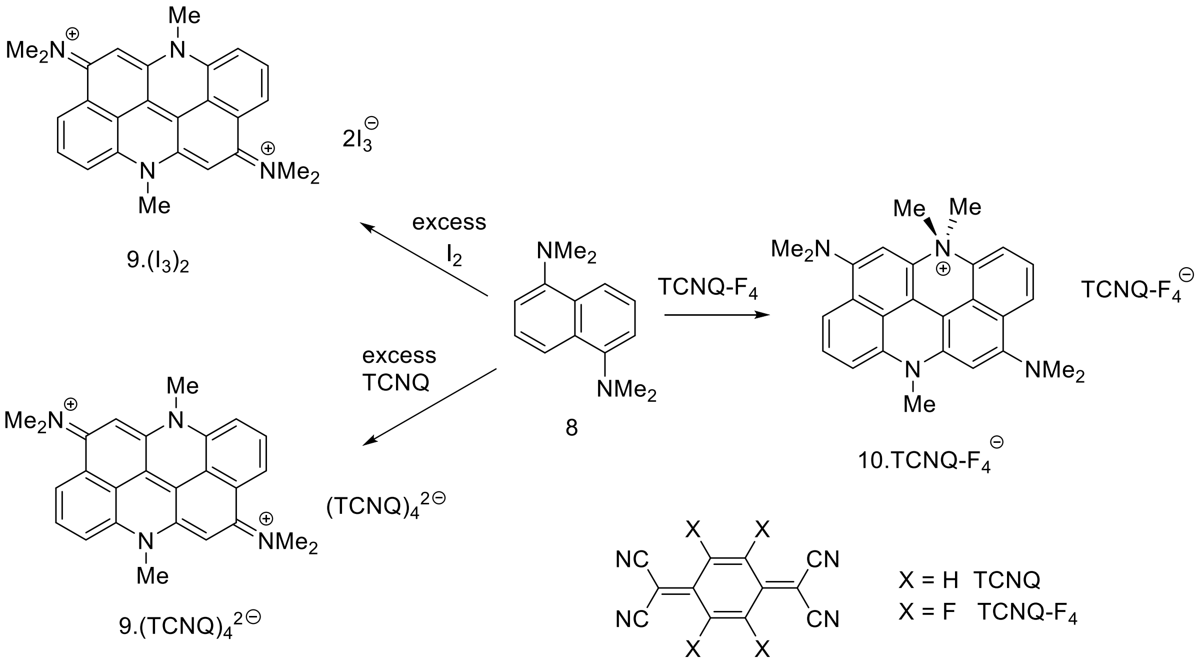
# Introduction.

Large, conjugated, aromatic hydrocarbons composed of fused benzene rings, representing a fragment of graphene are potential conducting materials for molecular electronics. Among these, derivatives of dibenzo[*def,mno*]chrysene, **1**, containing six fused benzene rings, has found potential for use in energy storage materials, solar cells and electroluminescent cells.[1] For example, push-pull dyes such as **2** containing this ring system have been assessed for use in solar cells and shown efficiencies > 5%.[2] Substitution of two carbons in **1** with nitrogens gives the diaza analogue **3**, which can be seen as two acridines fused back to back, or more precisely as an acridino[2,1,9,8-*klmna*]acridine. A reduced version of this ring system is **4**, which allows for two N-substitutions on the ring system, and derivatives such as **5** and **6**, and also the *bis*(diarylamino) derivative **7**, have been reported in the patent literature as having potential application in electroluminescent devices and as semiconductors for thin film transistors.[3] The synthesis of the hexyl derivative **5** starts with the self-coupling of 8-acetylamino-2-naphthol, but involves several further steps. Molecules based on **4** with further fused benzene rings have been reported as potential energy storage materials[4] and also for use in OLEDs.[5] Here we report the remarkable direct oxidation of 1,5-*bis*(dimethylamino)naphthalene **8** to the dication **9**, which contains the *bis* N-methylated derivative of **4** as a core and bearing two dimethylamino substituents to stabilise the charge. The naphthalene **8** has also been oxidized to the monocation **10**, in which the positive charge is located at a quarternary heterocyclic N atom.



*Scheme 1.* Structural diagrams **1**-**7**.

## Results and Discussion



*Scheme 2.* Synthesis of dication **9** and monocation **10**.

Treatment of 1-,5-*bis*(dimethylamino)naphthalene **8** with iodine in pyridine and 1,4-dioxane at room temperature for 12 hours, followed by addition of water, gave a dark precipitate of the *bis* triiodide salt of the dication **9** in high yield (82%) in a quite remarkable chemical reaction (Scheme 2). Two molecules of **8** have coupled through carbon atoms *para* to one dimethylamino group and then the second dimethylamino groups have ring closed on to adjacent *meta* positions from opposite molecules, with loss of a N-methyl group in each case, to form the dication **9**. The same product is obtained, in lower yield (57 %), if **8** is treated with N-iodosuccinimide.

The molecular structure of **9**.$(I_3)_2$ was determined by X-ray crystallography. The crystal structure of **9**.$(I_3)_2$ is triclinic, space group *P*-1, and the unit cell contains one dication, which is located on a centre of symmetry, and two triiodide anions which are centrosymmetrically related (Fig. 1 and Fig. S1). In dication **9** the two peripheral dimethylamino groups adopt a bonding geometry near to planar, with a sum of angles at the nitrogen atom of 357.5$^o$, so that their lone pairs can stabilise the 2+ charge on the ring system. The $Me_2N$-C bonds are thus shortened to 1.337(7) Å. However, there is steric repulsion between each dimethylamino group and its neighbouring *peri* hydrogen atom leading to a lengthening of the intervening ring C,C bond attached to the nitrogen to 1.470(7) Å at both sides of the molecule, the longest C,C bonds in the ring system (Fig. 2). This repulsion also leads to a small twist about the long axis of the hexacyclic system (Fig. 1, right), as well as preventing perfect planar bonding at the dimethylamino groups. The stretching of the two bonds to 1.470 Å is accompanied by lengthening of parallel C,C bond in the ring system but by lesser amounts (Fig. 2). The twist leaves each dimethylamino nitrogen atom displaced by 0.433 Å to one side of the best plane of the dication, while the adjacent unsubstituted fused benzene ring moiety is twisted to the other side with the largest carbon atom displacement from the best plane of 0.161 Å. The bonding geometry at the heterocyclic $N-CH_3$ group is exactly planar, and the two ring N-C bonds have lengths of 1.368(7) and 1.394(7) Å, with the $N-CH_3$ bond being 1.467(7) Å. In the crystal structure the dications and triiodide ions are packed in alternate layers along the *c* axis (Fig. S1).

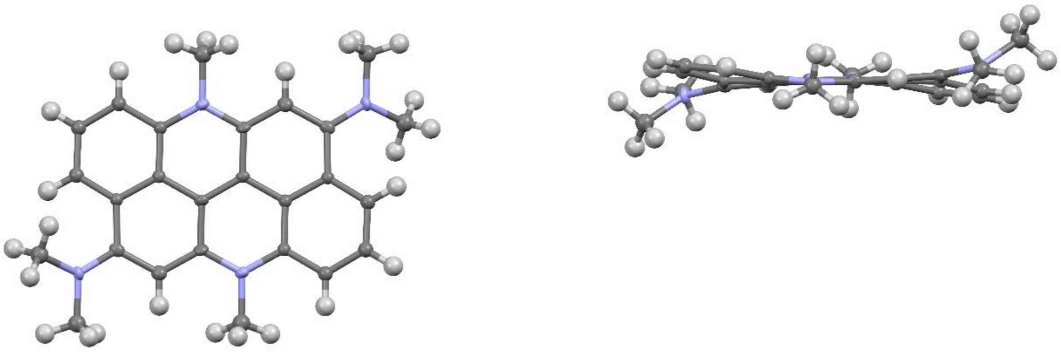


Fig. 1. Structure of dication **9** face-on (left) and edge-on (right).

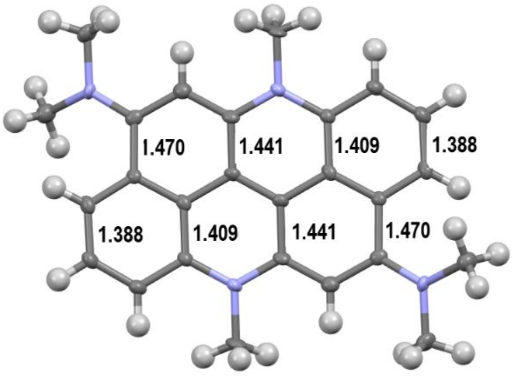
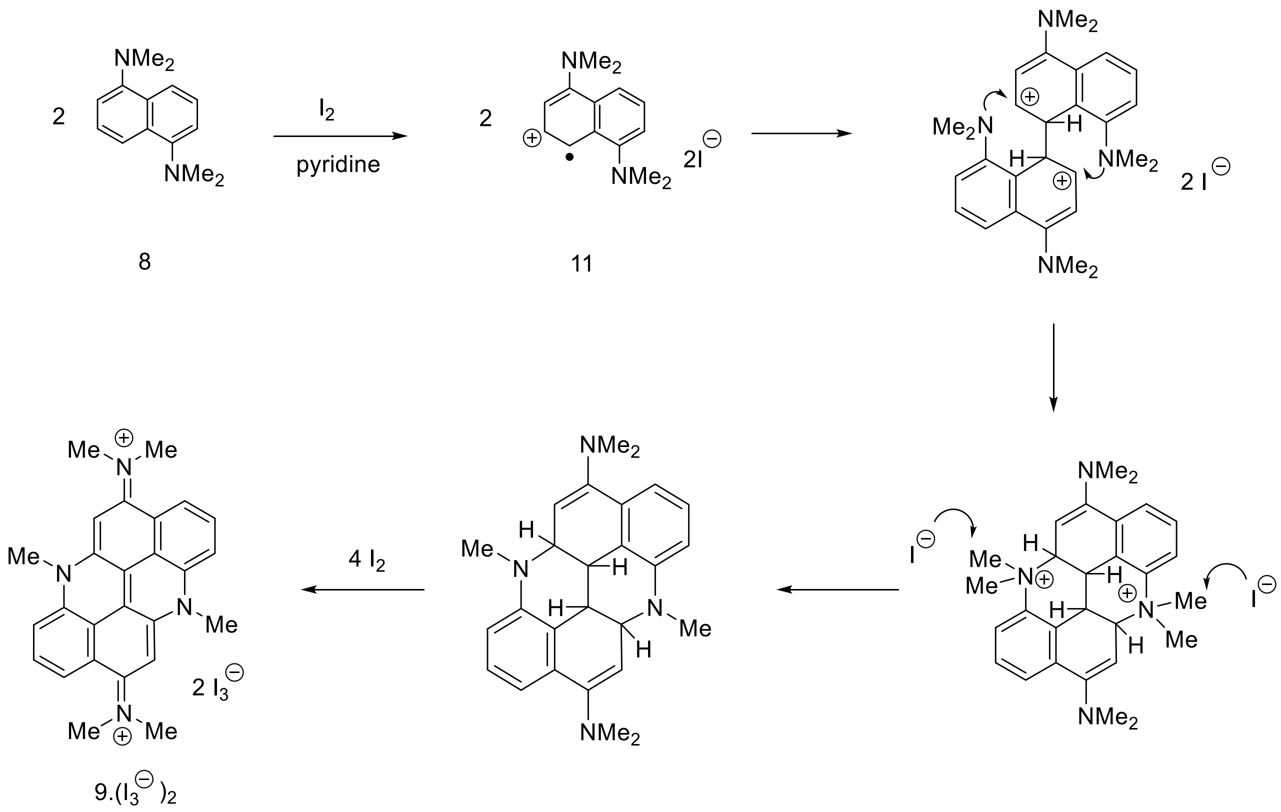


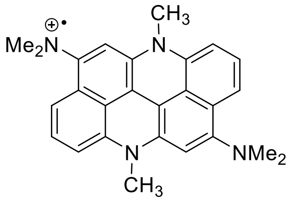
Fig. 2. Selected carbon-carbon bond lengths in dication **9**, e.s.d.s (0.007-0.008 Å), showing the effects of the pair of *peri*-repulsions.



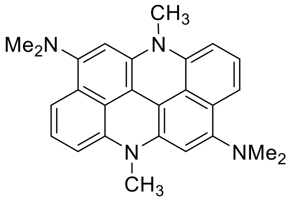
*Scheme 3.* Possible mechanism for the formation of **9**.$(I_3)_2$ from **8** and iodine.

A possible mechanism for the reaction is shown in Scheme 3. The first step is the formation of the radical cation **11**, probably by reaction with the iodopyridinium cation, which then dimerises by formation of the bond between the two radical centres *para* to the dimethylamino groups. The second set of dimethylamino groups then react with the cationic centres with loss of a methyl group. Oxidations then complete the formation of dication **9**.

Calculations at the UB3LYP/6-31g(d,p) level[6] on the singlet and triplet states of the isolated dication **9** suggest that the singlet structure is 1.29 eV more stable. The calculations also support the particularly long (N=C)C-C *peri* bond with a value of 1.473 Å, *cf.* the crystallographically determined value of 1.470 Å, the slight twist about the short axis of the molecular system, and the almost planar bonding geometry of the dimethylamino group. Cyclic voltammetry measurements on **9**.$(I_3)_2$ in 0.1 M n-$Bu_4NPF_6$ showed a reversible reduction peak at -0.56 V relative to Ag/AgCl. Thus, calculations were also carried out on two reduced species from dication **9**: the radical cation **12** and the neutral molecule **13**. Results for **9**, **12** and **13** are summarised in Table S1 in the ESI. Most notably, in the neutral species the dimethylamino groups now have pyramidal structures at nitrogen and are oriented to have one methyl group lying roughly perpendicular to the hexacyclic structure. This reduces the *peri* repulsion between a hydrogen and the dimethylamino group, and the resultant distortion of nearby bonds is reduced. The calculated structure of the radical cation **12** is intermediate between those of the dication and the neutral molecule with the dimethylamino group partially pyramidalised (sum of angles 351.9°).



12



13

The naphthalene **8** was treated with several other oxidizing agents (Scheme 2). Refluxing with TCNQ in acetonitrile gave crystals of the salt of the dication **9** with four TCNQ species as determined by X-ray crystallography (Fig. 3). The dication **9** is packed at *ca*. 57° to a block of four, almost parallel, TCNQ species which must bear an overall charge of -2. These four acceptor molecules lie in a slipped stacking arrangement, with the first two related to the second two by a centre of symmetry. The charge carried by each TCNQ can be estimated from its bond lengths, related to the effects of occupation of the LUMO orbital,[7] and this indicates that the central two TCNQs carry about twice as much charge as the outer pair. Furthermore, two distinct C≡N stretches are seen in the infra-red spectrum (2185 and 2154 cm$^{-1}$). The next block of four TCNQs along the *b* axis is strongly slipped with respect to its neighbour. Initial investigations of the electrical properties of both these salts of **9** suggest they are insulators.

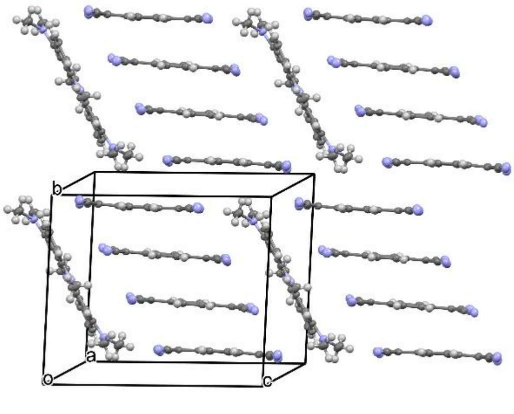


Fig. 3. Crystal packing arrangement for **9.(TCNQ)$_4$$^{2-}$** showing the stacking of groups of four TCNQ species along the *b* axis, the dication **9** is side-on.

In contrast, treatment of the diamine **8** with TNCQ-F$_4$ led to the salt of a related monocation **10**, as determined by X-ray crystallography (Fig. 4). Full details of molecular geometry are in Table S2. The new cation **10** has its positive charge localised at one quartenary ring nitrogen atom which bears two methyl groups. The dimethylamino groups are not involved in delocalising the positive charge, and so the $Me_2N$-C bonds to the heterocyclic system (1.405(2) and 1.419(2) Å) are longer than in the dication **9** and these dimethylamino groups have pyramidal geometry (sum of angles: 338.7 and 341.8°). This leads to less distortion of the ring system due to reduced *peri*-repulsion with the adjacent hydrogen atom. At the dimethylated ring nitrogen atom the four long N-C bonds (1.509-1.518 Å) are typical of a quarternary nitrogen, while at the neutral monomethylated nitrogen atom the endocyclic bond lengths (1.392 and 1.395 Å) indicate involvement of the nitrogen lone pair in the conjugated system. Calculations at the UB3LYP/6-31g(d,p) level lead to a very similar geometry for this cation (Table S2). The bond lengths of the TCNQ-$F_4$ species are consistent with it carrying a charge of *ca.* -1.[8] In the crystal structure pairs of cations and pairs of TCNQ-$F_4$ radical anions are packed alternately along an axis (Fig. 4). The TCNQ-$F_4$ radical anions lie parallel at a separation of 3.116 Å, and the centroid of a TCNQ-$F_4$ radical anion lies at 3.389 Å from the best plane of the cation.

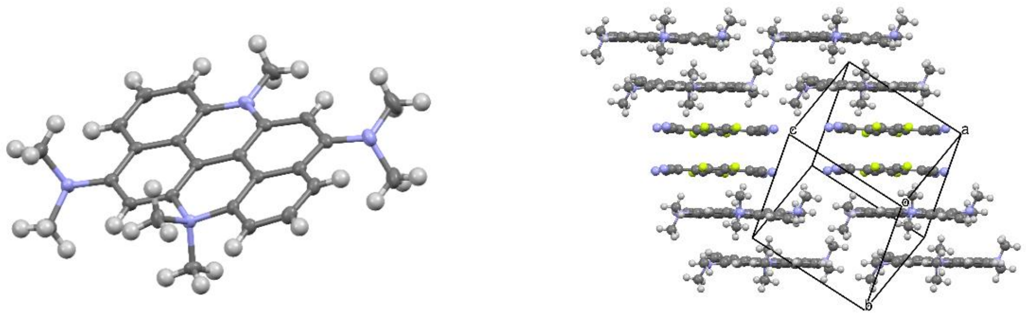


Fig. 4. Molecular structure of monocation **10** showing the heterocyclic positively charged nitrogen bearing two methyl groups (left); crystal structure of **10.TCNQ-$F_4$** showing the stacking of pairs of monocations **10** with pairs of TCNQ-$F_4$ anions (right).

In summary, treatment of 1,5-*bis*(dimethylamino)naphthalene with iodine yields an acridino[2,1,9,8-*klmna*]acridine derived dication in high yield. Further investigations show that treatment with TCNQ gives the same dication while treatment with TCNQ-$F_4$ gave an alternative monocation with the charge located on a ring nitrogen. The one step synthetic procedure using iodine opens up a direct route into preparing this hexacyclic ring system from a readily available naphthalene derivative, and thus provides opportunities to develop the chemistry of this system to provide new materials for use in electroluminescent materials and as semiconductors.

## Experimental.

**General.** Solution NMR spectra were measured on a Jeol ECLIPSE 400 spectrometer at 400 MHz for $^{1}H$ and at 100.6 MHz for $^{13}C$ using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling on solids or oils and are reported in $cm^{-1}$. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. **Note:** there is a report of the carcinogenicity of the parent heterocycle **3**.[9]

### Preparation of 9.$(I_3)_2$

Pyridine (12 ml) and iodine (2.19 g, 8.63 mmol) were added to a solution of 1,5-bis(dimethylamino)naphthalene (0.60 g, 2.80 mmol) in 1,4-dioxane (12 ml), and the resulting mixture was stirred overnight. Water (60 ml) was added to the mixture and the dark precipitate collected and washed with water and ethanol thoroughly and dried under vacuum to give bis triiodide **9.$(I_3)_2$** (1.33 g, 82 %) as a blue powder, m.p. 259-261 °C. $\delta_H$ (400 MHz, DMSO-$d_6$): 8.94 (2H, d, J = 8.8 Hz, 2×Ar-*H*), 8.83 (2H, d, J = 7.6 Hz, 2×Ar-*H*), 8.49 (2H, t, J = 8.4 Hz, 2×Ar-*H*), 7.31 (2H, s, 2×Ar-*H*), 4.61 (6H, s, 2×N-C$H_3$), 3.76 (12H, s, 2×N(C$H_3$)$_2$); $\delta_C$ (100 MHz, DMSO-$d_6$): 160.1, 144.2, 137.7, 132.4, 127.9, 123.1, 121.3, 120.2, 115.1, 98.1 (20×Ar-*H*), 45.8 (2× N($CH_3$)$_2$), 38.2 (2×N-$CH_3$); $\nu_{max}/cm^{-1}$: 2934, 2925, 2858, 1502, 1473, 1463, 1395, 1288, 1244, 1220, 1211, 1025, 825, 770, 761, 738, 644, 534. Found: C, 27.13; H, 2.26, N 4.89%. Calc. for $C_{26}H_{26}I_6N_4$: C, 27.02; H, 2.27, N 4.85%.

### Preparation of 9.(TCNQ)$_4$

A solution of 1,5-bis(dimethylamino)naphthalene (10 mg) and TCNQ (10 mg) in acetonitrile (15 ml) was heated at reflux for 20 h., and then the solvent was left to evaporate slowly. The residue was washed with DMF and ether to leave almost black crystalline blocks of **9.(TCNQ)$_4$** (5 mg), m.p. 175-178 °C, $\nu_{max}/cm^{-1}$: 3051, 2185, 2154, 1568, 1504, 1476, 1440, 1344, 1276, 1174, 970, 858, 833, 784, 748, 690, 539, 473.

### Preparation of 10.TCNQ-$F_4$

A solution of 1,5-bis(dimethylamino)naphthalene (9 mg) and TCNQ-$F_4$ (10 mg) in acetonitrile (15 ml) was heated at reflux overnight. The solution was then left to evaporate slowly. The residue was washed with DMF and ether to give small black parallelopipeds (4 mg), m.p. > 330 °C, $\nu_{max}$/cm$^{-1}$: 3054, 2228, 2193, 2178, 1584, 1545, 1516, 1506, 1391, 1354, 1339, 1319, 1182, 1138, 1004, 964, 860, 826, 811, 749, 473.

### X-ray Crystal Structures.

Full details of crystal data and methods are given in the ESI. Structures **9**.$(I_3)_2$, **9**.$(TNCQ)_4$, and **10**.TCNQ-$F_4$ have been deposited at the Cambridge Crystallographic Data Centre with reference numbers: CCDC -1951224-1951226.

### Conflicts of Interest.

There are no conflicts to declare.

### Acknowledgements.

We thank Nottingham Trent University for financial support.

### References.

1. P. I. Lazarev, Pavel Ivan, PCT Int. Appl. (2016), WO 2016187584 A1 20161124; P. Stoessel, A. H. Parham, C. Pflumm, A. Jatsch, J. Kaiser, PCT Int. Appl. (2015), WO 2015135624 A1 20150917.
2. Y. Geng, C. Yi, M. P. Bircher, S. Decurtins, M. Cascella, M. Grätzel, S.-X. Liu, *RSC Advances*, **2015**, *5*, 98643-98652.
3. B.-W. Park, Y.-H. Kwak, S.-Y. Lee, C.-H. Lee, S.-J. Cho, U.S. Pat. Appl. Publ. (2013), US 20130112946 A1 20130509; A. Wigglesworth, Y. Wu, P. Liu, Ger. Offen. (2012), DE 102012201973 A1 20120816.
4. J. Chisaka, M. Tamano, Jpn. Kokia Tokkyo Koho (2016), JP 2016178060 Q 20161006.

5. K. Kotwica, P. Bujak, P. Data, W. Krzywiec, D. Wamil, P. A. Gunka, L. Skorka, T. Jaroch, *Chem. Eur. J.*, **2016**, *22*, 7978–7986.
6. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, 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, Inc., Wallingford CT, 2016.
7. T. J. Kistenmacher, T. J. Emge, A. N. Bloch, D. O. Cowan, *Acta Crystallogr.* **1982**, *B38*, 1193-1199; X. Chi, C. Besnard, V. K. Thorsmølle, V. Y. Butko, A. J. Taylor, T. Siegrist, A. P. Ramirez, *Chem. Mater.*, **2004**, *16*, 5751-5755.
8. P. Hu, H. Li, Y. Li, H. Jiang, C. Kloc, *CrystEngComm*, **2017**, *19*, 618–624.
9. L. Bahna, V. Podany, A. Godal, *Neoplasma*, **1971**, *18*, 591-597.