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Structural and solvatochromic studies of a series of tricyanoquinodimethane-based zwitterions

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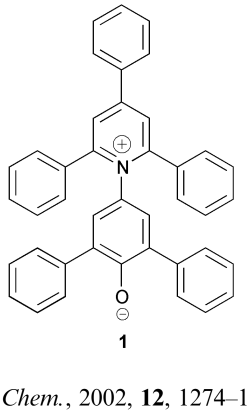
The synthesis and characterization of three new solvatochromic tricyanoquinodimethane zwitterionic systems is reported. (*Z*)-{β-[*N*-(1-Propyl)benzothiazolium-2-yl]-α-cyano-4-styryl}dicyanomethanide, C_3H_7(2)BT3CNQ, (*Z*)-{β-[*N*-(1-propyl)benzothiazolium-2-yl]-α-cyano-4-(2,3,5,6-tetrafluorostyryl)}dicyanomethanide, C_3H_7(2)BT3CNQF$_4$, and (*Z*)-{β-[*N*-(1-butyl)benzoselenazolium-2-yl]-α-cyano-4-styryl}dicyanomethanide, C_4H_9(2)BS3CNQ, exhibit negative solvatochromism, consistent with a transition from an ionic ground state to a significantly less polar excited state. X-Ray crystallography measurements confirm the zwitterionic ground state of these novel T3CNQ-based chromophores. The solvatochromic properties of these compounds are compared to those of a series of related quinolinium/pyridinium adducts, and also with those of the Reichardt betaine dye.

Introduction

Of the many compounds that exhibit some degree of solvatochromism, Reichardt's pyridinium *N*-phenoxide zwitterionic dye **1**[1] is distinguished for its exceptionally large negative solvatochromic effect in solvents of increasing polarity, and for the wide range of solvatochromic shifts exhibited. The longest wavelength intramolecular charge-transfer absorption band is hypsochromically (blue) shifted by $-9730\ \mathrm{cm}^{-1}$ (357 nm) on going from diphenyl ether ($\lambda_{\max} = 810$ nm) to water ($\lambda_{\max} = 453$ nm). The Reichardt dye and related compounds have attracted a plethora of interest as indicators of solvent polarity,[2] and also because they exhibit other phenomena such as halochromism, piezochromism and chiro-solvatochromism.[3] Compounds exhibiting solvatochromism are also of potential as materials which may exhibit the phenomenon of optical non-linearity under the appropriate conditions. One such class of compounds is the tricyanoquinodimethane-based zwitterion which has been extensively studied in terms of its non linear optical properties,[4,5] with the $C_{16}H_{33}$(4)Q3CNQ **2** adduct being shown to be truly multifunctional displaying such properties as molecular rectification[6] and photochromic behaviour.[7] In stark contrast the tricyanoquinodimethane (T3CNQ) adducts have received scant attention, as solvent polarity indicators with only a few examples being described.[8]



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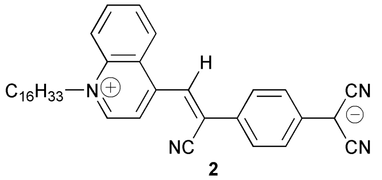
In this paper we report the synthesis and characterization of three new types of solvatochromic systems, the benzothiazolium-based chromophores, incorporating electron acceptors such as TCNQ **3** and TCNQF$_4$ **4**, and a related selenium analogue **5** which also exhibits a pronounced negative solvatochromic response. A comparison of the properties of **3**, **4** and **5** with those of the related *N*-methylpyridinium **6** and *N*-methylquinolinium **7** chromophores is also presented.

Few TCNQ-based chromophores appear to have been described in terms of their solvent polarity indicating abilities. The dipolar system **8**[8] appears to be the only TCNQ-based system extensively studied in terms of solvatochromic effects and shows a very limited response when compared to the Reichardt betaine **1**. Despite the extensive range of functionalised TCNQ compounds available, very few appear to have been utilised in the preparation of novel D–π–A solvatochromic systems. As part of our research programme into functionalised TCNQ-derivatives we have prepared a range of



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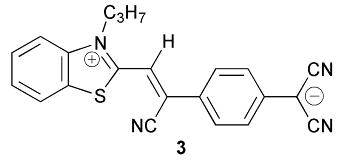

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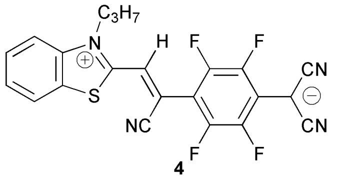

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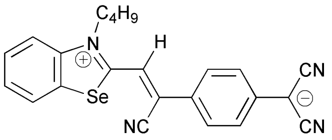

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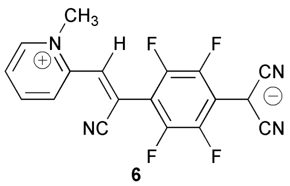

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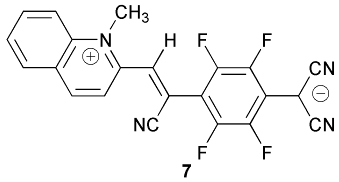

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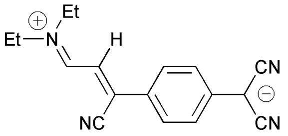

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novel D–π–A solvatochromic systems, incorporating not only functionalised electron acceptors such as tetramethyl-TCNQ (TMTCNQ)[9] and tetrafluoro-TCNQ ($TCNQF_4$), but also novel donor moieties such as the *N*-alkylated benzoselenazolium heterocycles. The introduction of such side groups (*i.e.* methyl and fluoro) into the backbone of D–π–A compounds has been shown to markedly affect both their physical and optical properties.[10]

Results and discussion

The synthetic route towards benzoselenazolium zwitterions such as **5** is shown in Scheme 1. The *N*-alkylated heterocyclic precursors **9** were easily accessible from Menschutkin type reactions of the appropriate haloalkane with the corresponding nitrogen heterocycle in acetonitrile. Conversion to the corresponding zwitterions **10** was accomplished under mild conditions in refluxing acetonitrile or chlorobenzene on treatment of the quaternised salt **9** with either TCNQ or $TCNQF_4$ in the presence of *N*-methylpiperidine. The resulting Knoevenagel condensation reaction and subsequent recrystallisation from acetonitrile led to the isolation of the adducts **10** as emerald green or deep red solids.

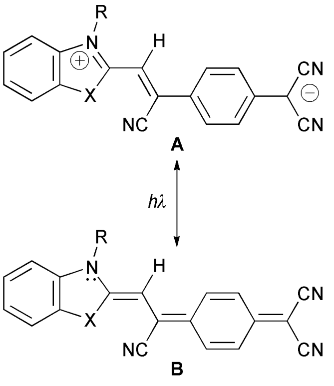
All of the zwitterions exhibited negative solvatochromism in solution, the position of the visible absorption band moving towards shorter wavelengths as the solvent polarity increases (Table 1). For example, the fluorinated $C_3H_7(2)BT3CNQF_4$ adduct **4** shows an absorption maximum shift of $\Delta\lambda = 174$ nm on going from chlorobenzene ($\lambda_{max} = 804$ nm) to methanol ($\lambda_{max} = 630$ nm), thus giving a maximum frequency range of *ca.* $-3435\ cm^{-1}$, approximately a third that of the Reichardt dye. The observation of negative solvatochromism reflects the stabilization of the charge-separated ground state **A**, relative to the neutral excited state **B**.

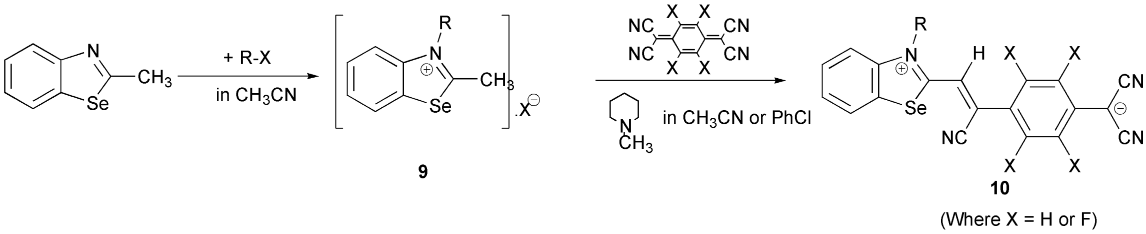
Table 1 Long-wavelength UV–Vis absorption maxima of zwitterions **3**, **4**, **5**, **6** and **7** in solvents of varying polarity

Solvent	ε_r	**3** λ_{max}/nm	**4**	**5**	**6**	**7**
Methanol	32.66	722	630	734	490	592
DMSO	46.45	734	636	750	492	552
DMF	36.71	748	652	776	504	566
Acetonitrile	35.94	738	664	786	510	570
Nitromethane	35.87	732	672	790	514	570
Acetone	20.56	786	686	796	532	596
Dichloromethane	8.93	814	766	820	575	638
THF	7.58	812	762	818	560	618
Chlorobenzene	5.62	824	804	828	540	604

The presence of the fluoro-substituents within the $T3CNQF_4$ ring system clearly shifts the absorption maximum to shorter wavelengths, when compared to the T3CNQ-based analogue **3**. This suggests that the extra electron-withdrawing moieties on the $T3CNQF_4$ part of the molecule hamper the back charge-transfer from A^- to D^+, thus shifting the absorption band to higher energy relative to the T3CNQ-based analogue. For each of these compounds, a plot of the wavenumber relating to the longest wavelength visible absorption band against the normalized solvent polarity parameter E^{N}_{T} for the Reichardt betaine dye (Fig. 1) reveals a negative solvatochromic response which correlates reasonably well with that observed for the Reichardt betaine.[2,3]

Although the $C_3H_7(2)BT3CNQ$ adduct **3** exhibits only a relatively small solvatochromic response of just $\Delta\bar{\nu} = -1714\ cm^{-1}$ ($\Delta\lambda = 102$ nm), on going from chlorobenzene ($\lambda_{max} = 824$ nm) to methanol ($\lambda_{max} = 722$ nm (Table 1)), the nature of the solvent–solute interactions observed is unusual in that the charge-transfer absorption band undergoes significant structural changes with decreasing solvent polarity. For example in high polarity solvents, such as DMSO/DMF/CH_3NO_2 *etc.*, the absorption maximum shows the usual broad topped transition associated with such compounds. In acetone, however the CT





Scheme 1

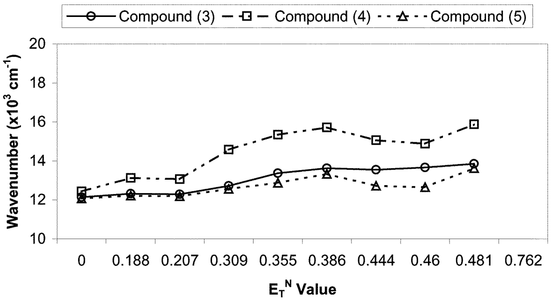


Fig. 1 Plot of wavenumber of longest-wavelength visible absorption band of the zwitterionic adducts **3**, **4** and **5**.

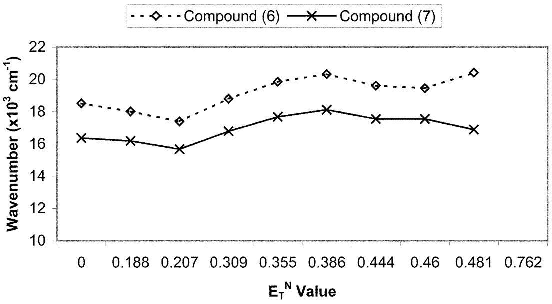


Fig. 3 Plot of wavenumber of longest-wavelength visible absorption band of the zwitterionic adducts **6** and **7**.

absorption band shows signs of band splitting (Fig. 2a). As the solvent polarity is decreased further the splitting increases until two distinct bands are observed in chlorobenzene (Fig. 2b). This splitting of the absorption band has been observed before in stilbazolium betaines[11] and is attributed to solvent induced broadening of the electronic transitions resulting in the loss of the coarse structure.

This anomaly is also observed in the corresponding benzoselenazolium adduct **5**, which shows band splitting in solvents of low polarity. Again as with the benzothiazolium analogue, compound **5** exhibits only a relatively small solvatochromic shift of $\Delta\bar{\nu} = -1546$ cm^{-1} ($\Delta\lambda = -94$ nm) on going from chlorobenzene ($\lambda_{max} = 828$ nm) to methanol ($\lambda_{max} = 734$ nm (Table 1)). It is of interest to note that the introduction of the more electropositive selenium atom into the aromatic donor moiety clearly shifts the absorption band to longer wavelengths as a result of a lowering in the charge-transfer energy barrier, hence illustrating that by careful manipulation the CT absorption band can be finely tuned.

It was of interest to compare the solvatochromic properties of the above zwitterions with those of the fluorinated *N*-methylpyridinium, $CH_3(2)P3CNQF_4$ **6**, and *N*-methylquinolinium, $CH_3(2)Q3CNQF_4$ **7** analogues. Prepared in a similar fashion to **3**, **4** and **5** (Scheme 1), compounds **6** and **7** were found to have a similar solvatochromic response (Table 1) with a maximum frequency range of $\Delta\bar{\nu} = -3017$ cm^{-1} ($\Delta\lambda = 85$ nm) observed on going from dichloromethane ($\lambda_{max} = 575$ nm) to methanol ($\lambda_{max} = 490$ nm) for compound **6**. Although the solvatochromic responses for **6** and **7** are considerably smaller than that exhibited by the Reichardt betaine **1**, in solvents of low polarity evidence of reverse solvatochromism is observed.[12] This is in stark contrast to the fluorinated adduct $C_3H_7(2)BT3CNQF_4$ **4** which shows no such behaviour. A plot of the wavenumber for the longest-wavelength absorption band of **6** and **7** against the Reichardt $E^N{}_T$ parameters (Fig. 3) clearly reveals the significant trend to positive solvatochromism in the less polar solvents.

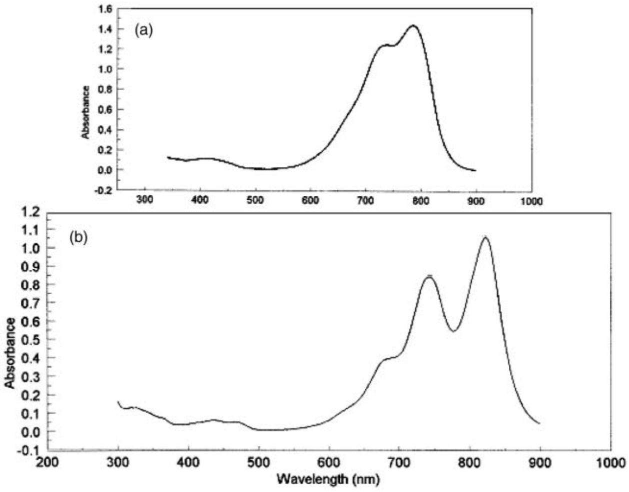


Fig. 2 Unusual behaviour of the $C_3H_7(2)BT3CNQ$ in (a) acetone and (b) chlorobenzene.

UV–Vis spectrophotometric studies conducted on the fluorinated analogues[10] has illustrated that at low concentrations the materials deviate from the Beer–Lambert law, thus suggesting aggregation of the zwitterions in solution. This assumption has been confirmed by Langmuir–Blodgett studies[10] and X-ray crystallography.

Solid state structure

The charge-separated ground state of these dipolar molecules has been confirmed by crystallographic studies carried out on $C_3H_7(2)BT3CNQF_4$ **4** and $C_4H_9(2)BS3CNQ$ **5**. The T3CNQ-based benzoselenazolium analogue **5**[†] (Fig. 4a) crystallises in the space group $P\bar{1}$ with two molecules per unit cell. Comparison of the C19–C20 (1.362(4) Å), C16–C17 (1.363(4) Å) and C12–C13 (1.385(4) Å) bond lengths with the predicted charge-separated ground state indicates the retention of some quinoid character in the solid state structure.

The $C_3H_7(2)BT3CNQF_4$ adduct **4**[‡] (Fig. 4b) crystallises in the space group $P2_1/c$. As a consequence of the highly dipolar nature of the zwitterions it forms centrosymmetric dimers (Fig. 5a). Additional intermolecular hydrogen bonds result in a 3D network structure (Fig. 5b) that is markedly different to the packing patterns observed for other documented TCNQ-based zwitterions.[13,14] Details of the various hydrogen bonds present in both compounds are shown in Table 2. Despite the introduction of highly electronegative fluorine substituents into the D–π–A framework, the extended C17–C20 (1.421(2) Å) and C12–C14 (1.457(2) Å) bonds and benzenoid nature of the acceptor ring, in which the C18–C19 (1.366(2) Å) and C15–C16 (1.365(2) Å) bonds show bond lengths somewhere in between that of a fully delocalised system (~1.39 Å) and a formal carbon–carbon double bond (~1.32 Å), clearly illustrate that some retention of quinoid character remains.

[†] *Crystal data for* **5**: $C_{23}H_{18}N_4Se$, $M = 429.37$, triclinic, $a = 8.0663(3)$, $b = 9.4561(2)$, $c = 12.8115(5)$ Å, $\alpha = 83.317(2)$, $\beta = 81.489(1)$, $\gamma = 89.601(2)°$, $U = 959.83(6)$ Å^3, $T = 150$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $\mu(\text{MoK}\alpha) = 1.972$ mm^{-1}, 12251 reflections measured, 3746 unique ($R_{int} = 0.0662$) which were used in all calculations. The final wR (F^2) was 0.0784 (all data) and the final R (F) was 0.0401 (observed data, $I > 2\sigma(I)$). CCDC reference number 176118. See http://www.rsc.org/suppdata/jm/b1/b111392p/ for crystallographic files in .cif or other electronic format.

[‡] *Crystal data for* **4**: $C_{22}H_{12}F_4N_4S$, $M = 440.42$, monoclinic, $a = 11.243(2)$, $b = 8.113(1)$, $c = 20.822(4)$ Å, $\beta = 101.537(3)°$, $U = 1860.8(6)$ Å^3, $T = 150$ K, space group $P2_1/c$ (no. 4), $Z = 4$, $\mu(\text{MoK}\alpha) = 0.231$ mm^{-1}, 20416 reflections measured, 4609 unique ($R_{int} = 0.0245$) which were used in all calculations. The final wR (F^2) was 0.0853 (all data) and the final R (F) was 0.0330 (observed data, $I > 2\sigma(I)$). CCDC reference number 176117. See http://www.rsc.org/suppdata/jm/b1/b111392p/ for crystallographic files in .cif or other electronic format.

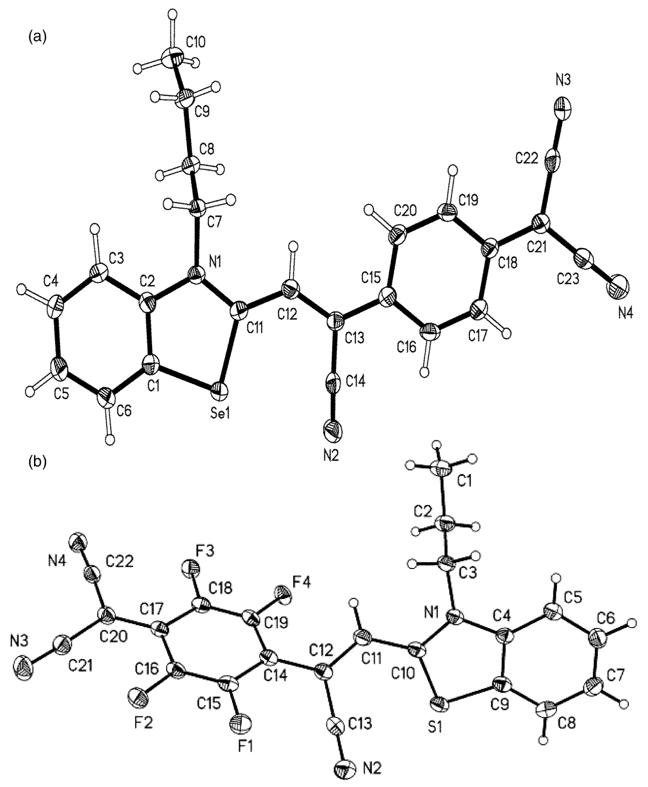


Fig. 4 (a) Solid state structure of C_4H_9(2)BS3CNQ **5**; (b) solid state structure of C_3H_7(2)BT3CNQF$_4$ **4**.

Charges within the zwitterion are assigned on the basis of the shortening of the C10–N1 (1.34(2) Å) bond and the fact that all the bond angles around N1 are between 113.8(11) and 124.2(11)°. The negative charge is considered to be delocalised over the dicyanomethanide unit and into the T3CNQ ring system. Such assignments, along with the retention of some quinoid character, do however emphasise the inadequacy of using conventional Kekulé structures to represent such species.

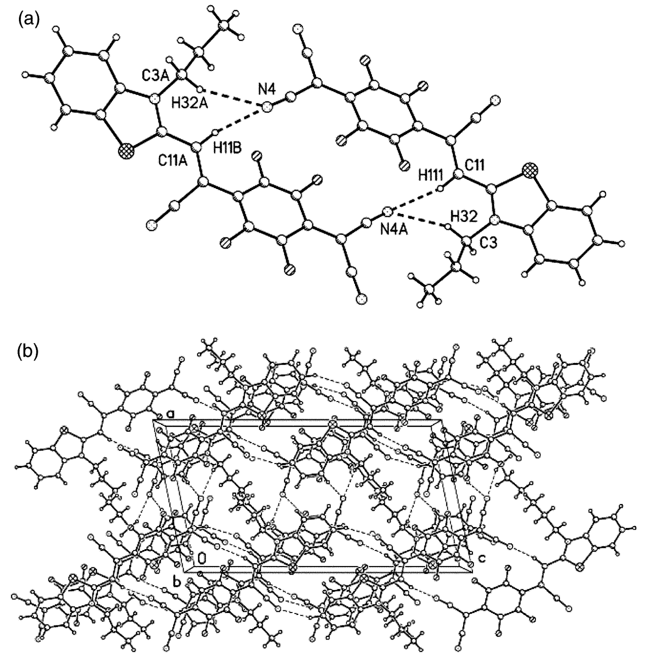


Fig. 5 (a) Dimer packing of C_3H_7(2)BT3CNQF$_4$ **4**; (b) 3-dimensional packing diagram of C_3H_7(2)BT3CNQF$_4$ **4**.

Table 2 Hydrogen bonds for **4** and **5** [Å and °]

D–H···A	d(D–H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/°
Compound **4**^{a}				
C(7)–H(71)···N(2)#1	0.958(18)	2.452(18)	3.347(2)	155.5(14)
C(3)–H(31)···N(3)#2	0.971(17)	2.535(17)	3.417(2)	151.0(13)
C(5)–H(51)···N(3)#2	0.927(17)	2.414(18)	3.316(2)	164.1(14)
C(3)–H(32)···N(4)#3	0.968(17)	2.650(16)	3.440(2)	139.0(13)
C(11)–H(111)···N(4)#3	0.932(18)	2.394(18)	3.235(2)	150.0(15)
Compound **5**^{b}				
C3−H3···N4^{i}	0.97(2)	2.32(3)	3.219(4)	152.8(19)
C7−H7A···N3^{ii}	0.99(2)	2.53(2)	3.400(3)	146.3(16)
C20−H20···N3^{ii}	0.95(3)	2.36(3)	3.283(4)	165(2)

^{a}Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 1, -z$; #2 $x - 1, -y + 3/2, z - 1/2$; #3 $-x + 2, -y + 1, -z + 1$. ^{b}Symmetry transformations used to generate equivalent atoms: (i) $x, y - 1, z + 1$ (ii) $-x + 1, -y + 2, -z$.

Conclusion

This paper describes the synthesis and characterisation of a series of three benzothiazolium or benzoselenazolium zwitterionic D–π–A adducts of TCNQ and TCNQF$_4$. All exhibit pronounced negative solvatochromism in solution, with the response correlating well with that observed for the Reichardt betaine, indicating their potential as indicators of solvent polarity. X-Ray crystallography has illustrated retention of quinoid character in the ground state, even when electron withdrawing fluorine substituents are incorporated. The intermolecular hydrogen bonds generated by the fluorinated benzothiazolium analogue result in a 3D network which is markedly different to the packing patterns observed in other documented zwitterions. The introduction of such functionality has also demonstrated that by careful manipulation the properties exhibited by such highly polarised species can be finely tuned.

Experimental

^{1}H and ^{19}F NMR studies were carried out using a Bruker AC250 FT-NMR Spectrometer. Mass spectra were recorded on a VG Micromass 7070F instrument. Infrared spectra were recorded on an ATI Mattson Genesis series FTIR instrument. Solvents were purified and dried by standard methods. Microanalytical data was obtained from Medac Limited at Brunel University.

Preparation of electron-donor intermediates

N-Methyl-2-methylquinolinium iodide,[15] 1,2-dimethylpyridinium iodide[16] and *N*-(1-butyl)-2-methylbenzoselenazolium iodide[15] were prepared by standard literature methods. *N*-(1-Propyl)-2-methylbenzothiazolium iodide was obtained commercially from Sigma-Aldrich.

Preparation of electron-acceptor intermediates

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (TCNQF$_4$) was prepared *via* a modified Wheland *et al.* method[17] from hexafluorobenzene. 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) was obtained commercially from Sigma-Aldrich.

(*Z*)-{β-[*N*-(1-Propyl)(benzothiazolium-2-yl]-α-cyano-4-styryl}-dicyanomethanide 3[18]

N-(1-Propyl)-2-methylbenzothiazolium iodide (0.78 g, 2.4 mmol), 7,7,8,8-tetracyano-*p*-quinodimethane (0.5g, 2.4 mmol) and *N*-methylpiperidine (0.05 g, 0.5 mmol) were refluxed in acetonitrile (30 cm^3) for 6 hours. The resulting green suspension was filtered and the recovered solid washed with diethyl ether (75 cm^3). No further purification was required to afford 0.52 g of emerald green powder (57%, mp > 300 °C).

IR (KBr): 2930 (C–H str), 2175 (C≡N str), 1601 (C=C str), 1496 (Ar C=C str) cm^{-1}. MS (EI): *m/z* = 368 (100%, M^+), 326 (96%, $M^+ - C_3H_6$), 299 (12%, M^+ − R − HCN), 289 [8%, M^+ − R − $C(CN)_2$]. UV/Vis (CH_3CN): λ_{max} = 738(CT) nm. $C_{22}H_{16}N_4S$(368.4), Calc: C 71.72, H 4.38, N 15.21, S 8.70%. Found: C 71.56, H 4.32, N 15.14, S 8.92%.

(*Z*)-{β-[*N*-(1-Propyl)benzothiazolium-2-yl]-α-cyano-4-(2,3,5,6-tetrafluorostyryl)}dicyanomethanide 4

N-(1-Propyl)-2-methylbenzothiazolium iodide (0.23 g, 0.72 mmol), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (0.2 g, 0.72 mmol) and *N*-methylpiperidine (0.07 g, 0.72 mmol) were refluxed in chlorobenzene (30 cm^3) for 3 hours. Upon cooling a green solid was deposited which was recrystallised from acetonitrile affording gold/green crystals: 0.170 g (54% yield, mp 304 °C).

IR (KBr): 2971, 2918 (C–H str), 2192, 2166 (C≡N str), 1631 (C=C str), 1496 (Ar C=C str), 1227 C–F str) cm^{-1}. ^{1}H NMR: (d_6-DMSO) δ = 1.0 (t, 3H, CH_3-R) 1.9 (m, 2H, R-CH_2) 4.9 (t, 2H, CH_2N^+) 8.0 (m, 2H, Ar-H) 8.35 (s, 1H, C=C-H) 8.5 (d, 1H, Ar-H) 8.6 (d, 1H, Ar-H). ^{19}F NMR: (d_6-DMSO) δ = −148.28, −148.31 (d, 2F, C-F), −143.09, −143.13 (d, 2F, C-F). MS (EI): *m/z* = 441 (5%, M^+), 415 (15%, M^+ − CN), 398 (16%, $M^+ - CH_3CN$), 378 [34%, $M^+ - C(CN)_2$]. UV/Vis (CH_3CN): λ_{max} = 332, 664(CT) nm. $C_{22}H_{12}N_4F_4S$(440.39), Calc: C 60.00, H 2.75, N 12.72, F 17.25, S 7.28%. Found: C 59.95, H 2.77, N 12.59, F 17.21, S 7.19%.

(*Z*)-{β-[*N*-(1-Butyl)benzoselenazolium-2-yl]-α-cyano-4-styryl}-dicyanomethanide 5

N-(1-Butyl)-2-methylbenzoselenazolium iodide (0.3 g, 0.96 mmol), 7,7,8,8-tetracyano-*p*-quinodimethane (0.20 g, 0.96 mmol) and *N*-methylpiperidine (0.095 g, 0.96 mmol) were refluxed in acetonitrile (50 cm^3) for 12 hours. Upon cooling to 2 °C for 48 hours the dark green precipitate was filtered off and recrystallised from acetonitrile affording fine light green crystals: 0.1 g (24% yield, mp > 300 °C).

IR (KBr): 2920 (C–H str), 2180, 2140 (C≡N str), 1650 (C=C str), 1550 (Ar C=C str) cm^{-1} MS (EI): *m/z* = 429 (70%, M^+), 374 (80%, $M^+ - C_4H_9$). UV/Vis (CH_3CN): λ_{max} = 786(CT) nm. $C_{23}H_{18}N_4Se$(429.3), Calc: C 64.34, H 4.23, N 13.05%. Found: C 64.14, H 4.25, N 12.98%.

(*Z*)-{β-(*N*-Methylpyridinium-2-yl)-α-cyano-4-(2,3,5,6-tetrafluorostyryl)}dicyanomethanide 6

1,2-Dimethylpyridinium iodide (0.34 g, 1.4 mmol), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (0.4 g, 1.4 mmol) and *N*-methylpiperidine (0.14 g, 1.4 mmol) were refluxed in acetonitrile (15 cm^3) for 5 hours. Upon cooling a red solid was obtained. The recovered solid was recrystallised from acetonitrile affording a brick red powder: 0.20 g (39% yield, mp 296 °C decomp).

IR (KBr): 2995 (C–H str), 2183, 2149 (C≡N str), 1625 (C=C str), 1586, 1491 (Ar C=C str), 1222 (C–F str) cm^{-1}. ^{1}H NMR: (d_6-DMSO) δ = 4.35 (t, 3H, CH_3N^+) 7.95 (s, 1H, C=C-H) 8.2 (t, 1H, Ar-H) 8.65 (d, 1H, Ar-H), 8.75 (t, 1H, Ar-H), 9.2 (d, 1H, Ar-H). ^{19}F NMR: (d_6-DMSO) δ = −148.42, −148.30 (d, 2F, C-F), −144.47, −144.35 (d, 2F, C-F). MS (EI): *m/z* = 356 (14%, M^+), 342 (46%, $M^+ - CH_2$), 329 (50%, M^+ − HCN), 323 (100%, $M^+ - CH_3F$). UV/Vis (CH_3CN): λ_{max} = 310, 510(CT) nm. $C_{18}H_8N_4F_4$(356.26), Calc: C 60.69, H 2.26, N 15.72, F 21.33%. Found: C 60.51, H 2.40, N 15.45, F 21.26%.

(*Z*)-{β-(*N*-Methylquinolinium-2-yl)-α-cyano-4-(2,3,5,6-tetrafluorostyryl)}dicyano methanide 7

N-Methyl-2-methylquinolinium iodide (0.20 g, 0.72 mmol), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (0.20 g, 0.72 mmol) and *N*-methylpiperidine (0.07 g, 0.72 mmol) were refluxed in acetonitrile (30 cm^3) for 3 hours. Upon cooling a black solid was obtained which was recrystallised from methanol affording a deep purple powder: 0.140 g (48% yield, mp > 300 °C).

IR (KBr): 2925, 2853 (C–H str), 2184, 2152 (C≡N str), 1635 (C=C str), 1496 (Ar C=C str), 1227 (C–F str) cm^{-1}. ^{1}H NMR: (d_6-DMSO) δ = 4.5 (t, 3H, CH_3N^+) 8.05 (d, 1H, Ar-H), 8.3 (s, 1H, C=C-H) 8.35 (t, 1H, Ar-H) 8.55 (d, 1H, Ar-H), 8.65 (d, 1H, Ar-H), 8.7 (d, 1H, Ar-H), 9.45 (d, 1H, Ar-H). ^{19}F NMR: (d_6-DMSO) δ = −147.7, −146.9 (d, 2F, C-F), −143.47, −142.56 (d, 2F, C-F). MS (EI): *m/z* = 406 (12%, M^+), 392 (92%, $M^+ - CH_2$), 379 (100%, M^+ − HCN), 327 [44%, M^+ − R − $C(CN)_2$]. UV/Vis (CH_3CN): λ_{max} = 570(CT) nm. $C_{22}H_{10}N_4F_4$(406.32), Calc: C 65.03, H 2.48, N 13.78, F 18.71%. Found: C 64.93, H 2.45, N 13.78, F 18.51%.

X-Ray crystallography

Single crystal structure determination of **4** was carried out from data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073) on a Bruker SMART-CCD 1K diffractometer (Durham University Chemistry Department) equipped with a Cryostream N2 flow cooling device.[19] Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a sphere of data to a maximum resolution of 0.75 Å. Cell parameters were determined and refined using the SMART software[20] from the centroid values of 512 reflections with 2θ values between 27° and 56°. Raw frame data were integrated using the SAINT program.[21] Reflection data were corrected by absorption and other effects, by the multi-scan method based on multiple scans of identical and Laue equivalent reflections, using the SADABS program.[22] (T_{min} = 0.855, T_{max} = 0.977) The structure was solved by Direct Methods using SHELXS-97[23] and refined by full-matrix least squares on F^2 using SHELXL-97.[24] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogens atoms were located from difference Fourier maps and their coordinates and isotropic adps were refined.

Single crystal structure determination of **5** was carried out from data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073) on an Enraf Nonius Kappa CCD diffractometer (EPSRC National Crystallography Service, Southampton University Chemistry Department) equipped with a Cryostream N2 flow cooling device.[19] Series of ϕ-scans and ω-scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.81 Å. Cell parameters were determined and refined using the DENZO program.[25] from the centroid values of 12468 reflections with 2θ values between 4° and 52°. Raw frame data were integrated using the DENZO program.[25] Reflection data were corrected by absorption and other effects, by the multi-scan method based on multiple scans of identical and Laue equivalent reflections, using the SORTAV program.[26] (T_{min} = 0.756, T_{max} = 0.827) The structure was solved by Direct Methods using the DIRDIF-96 program[27] and refined by full-matrix least squares on F^2 using SHELXL-97.[24] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogens atoms were initially placed in their geometrically ideal positions and their coordinates and isotropic adps were refined (except for H16, which was allowed to ride on their parent C atom at an idealized fixed C–H distance of 0.95 Å).

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