



Synthesis and optical properties of new tricyano-*p*-quinodimethane dyes: molecular and polymeric systems

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Abstract

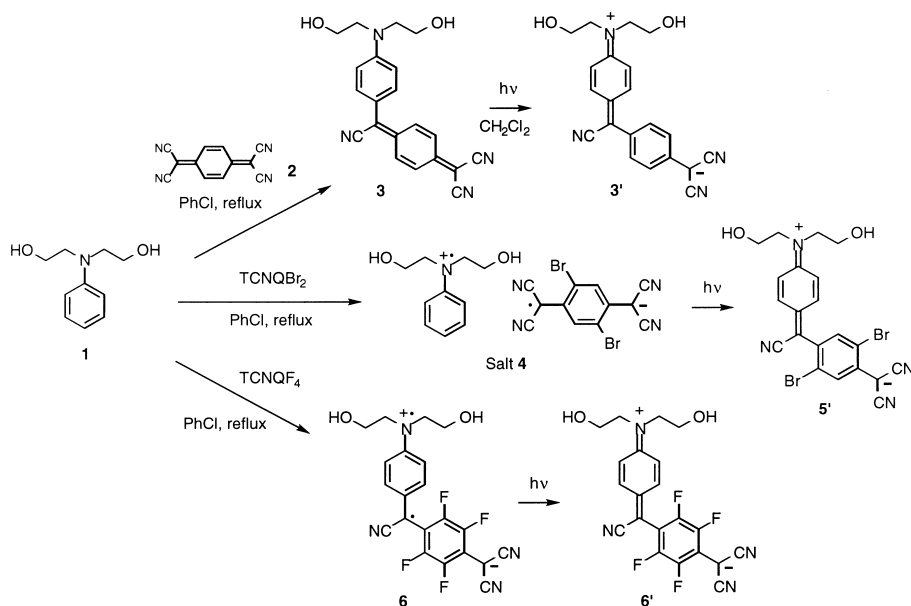
The reaction of *N,N*-bis(2-hydroxyethyl)aniline **1** with tetracyano-*p*-quinodimethane (TCNQ) **2** yields the photochromic red chromophore **3** [$\lambda_{\max}$ (acetone/dichloromethane) 497 nm] which upon UV irradiation is converted into the blue zwitterionic form **3'** ($\lambda_{\max}$ 680 nm) by a novel intramolecular charge transfer process involving a D-quinoid-aryl-A $\rightarrow$ D⁺-aryl-quinoid-A⁻ conversion. The analogous process occurs in the polyimide derived system **8**. Different products are isolated from reactions of **1** with the stronger electron acceptors TCNQBr₂ and TCNQF₄. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: tetracyano-*p*-quinodimethane; charge-transfer; photochromism; polyimides.

In the search for organic chromophores with electron accepting properties, derivatives of tricyanoethene (TCE)¹ and tricyano-*p*-quinodimethane (TCQ)² have attracted considerable attention, and some of these systems display high second order nonlinear optical effects.³ The TCQ systems offer the advantage of an extended π -system and gain in aromaticity upon charge transfer. Furthermore, the TCQ acceptor properties can be finely tuned by the electronic nature of substituents attached to the precursor tetracyano-*p*-quinodimethane (TCNQ) framework.⁴ Herein we report the synthesis and optical properties of new TCQ acceptor systems bearing an *N,N*-disubstituted aniline group to provide donor- π -acceptor chromophores. We have also varied the electron affinity of the TCQ moiety and embedded the chromophores within a polymer matrix.

We initially studied monomeric species, and in accord with other aniline derivatives,⁵ the reaction of *N,N*-bis(2-hydroxyethyl)aniline **1** with TCNQ **2** in chlorobenzene gave product **3**⁶ (51% yield, Scheme 1) as a red solid [$\lambda_{\max}$ (acetone/dichloromethane) 497 nm] formed by nucleophilic displacement of cyanide ion from TCNQ. Compound **3** is photochromic: upon irradiation with UV light (Xe lamp, using a CuSO₄ thermal filter) in dichloromethane solution, the colour changed to dark blue and a new absorption band emerged at $\lambda_{\max}$ 680 nm assigned to the zwitterionic structure **3'**.

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Scheme 1.

The conversion of **3** into **3'** is a novel photochemically-induced intramolecular charge transfer process in a donor- π -acceptor system, comprising the interchange of aromatic and quinoid systems (i.e. D-quinoid-aryl-A $\rightarrow$ D⁺-aryl-quinoid-A⁻). This process is fundamentally different from diquinoid $\rightarrow$ diaryl transformations (i.e. D-quinoid-quinoid-A $\rightarrow$ D⁺-aryl-aryl-A⁻) which are well documented, e.g. in diphenoquinoid derivatives.⁷

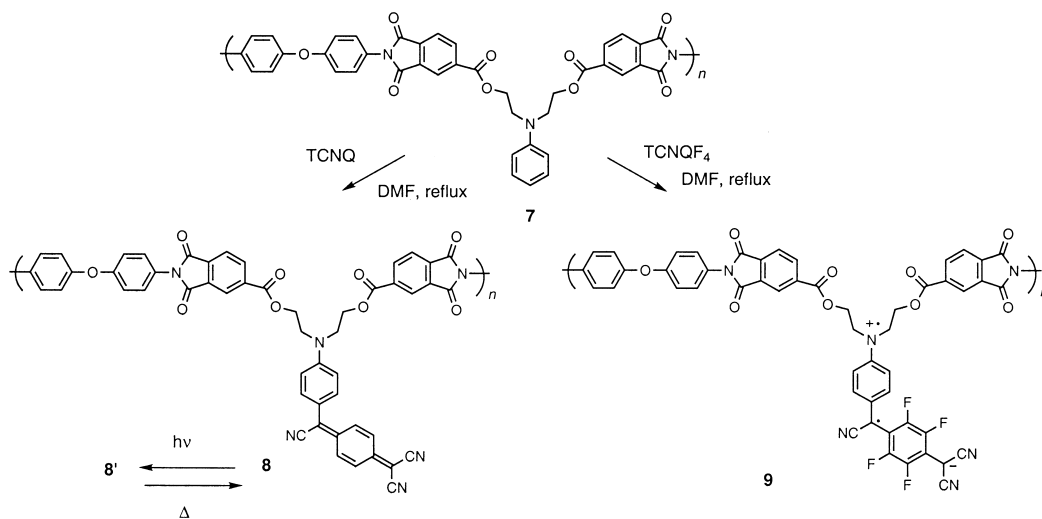
We have explored the analogous reactions of **1** with 2,5-dibromo- and 2,3,5,6-tetrafluoro-TCNQ: the electronegative halogen substituents increase the electron affinity relative to unsubstituted TCNQ (E_1 values: TCNQ +0.17, TCNQBr₂ +0.41, TCNQF₄ +0.53 V versus SCE in MeCN).^{4a} We reasoned that this effect should also apply to the TCQ moiety, thereby stabilising the zwitterionic state if analogues of **3'** could be obtained. The reaction of compound **1** with TCNQBr₂ and TCNQF₄ followed different courses from the reaction with TCNQ. With TCNQBr₂, instead of the red covalent analogue of **3**, a dark charge-transfer salt **4** was isolated (45% yield), comprising the anilinium cation radical and the TCNQBr₂ anion radical. EPR studies on salt **4** revealed a strong signal with a g value of 2.0028, which is typical of a TCNQ anion radical.⁸ UV irradiation of salt **4** in DMF afforded a blue covalent species (λ_{max} 680 nm) assigned the zwitterionic structure **5'** which was epr silent.

Reaction of **1** with TCNQF₄ under identical conditions used for TCNQ and TCNQBr₂ gave a stable yellow solid (45% yield, λ_{max} 460 nm) to which we assign the covalent zwitterionic diradical structure **6**. The compound gave a strong epr signal with a g value of 2.0026, and a spin concentration of two unpaired electrons per molecule [referenced to 1,1-diphenyl-2-picrylhydrazyl (DPPH)]. Compound **6** was converted into the blue zwitterionic compound **6'** (λ_{max} 685 nm; epr silent) on UV irradiation.

It is very interesting that the initial products isolated from the reactions of **1** with TCNQ, TCNQBr₂ and TCNQF₄ are different in each case. It is reasonable to propose that each reaction initially affords an intermolecular charge-transfer complex between **1** and the TCNQ acceptor, as

suggested earlier for the interaction of *N,N*-dimethylaniline with TCNQ,⁹ but the only complex of this type isolated in the present series of reactions is the TCNQBr₂ salt **4**. This is reminiscent of the unusually high stability of CT salts of TCNQBr₂, compared to the TCNQ and TCNQF₄ counterparts, observed in previous work with other electron donor molecules.¹⁰ The TCNQ and TCNQF₄ complexes of **1** react readily, with loss of HCN, to form the covalent products. This comparable reaction for **4** requires photochemical activation. The direct formation of structure **6** is a consequence of the very strong electron acceptor properties (i.e. high stability of the anion radical) of the TCQF₄ moiety.

We sought to attach covalently these new chromophores to a polymeric system with the aim of improving their processability and stability to photo- and oxidative degradation. Polyimides have been widely used as a backbone for pendant chromophores due to their ease of synthesis, solubility in organic solvents, good mechanical properties and high glass transition temperatures (*T_g*).^{1b,11} Polymer **7** reacted with TCNQ in DMF as above, to yield a red polymer **8** (Scheme 2) [90% yield, MW > 100,000, λ_{max} (DMF) 497 nm]. The *T_g* for polymer **7** was 156°C; for polymer **8** this value was raised to 175°C, and the solubility in organic solvents was significantly reduced. These observations can be attributed to functionalisation of the polymer.



By direct analogy with compound **3**, the irradiation of a solution of polymer **8** in DMF resulted in a blue solution (λ_{max} 680 nm) signifying conversion to the zwitterionic species **8'** (Fig. 1). Compounds **3'** and **5'** are stable for several weeks in solution and in the solid state; polymer **8'** reverts to **8** after a few days at 0°C; **8'** can be regenerated upon photolysis, and this cycle can be performed several times, without observable decomposition of **8** or **8'**.

Reaction of polymer **7** with TCNQBr₂ yielded an insoluble polymeric CT salt,¹² which was unchanged upon UV irradiation. Reaction of polymer **7** with TCNQF₄ gave a yellow polymer **9** (90% yield) analogous to monomer **6**, which (in contrast to **6**) was unchanged upon UV irradiation. Clearly the polyimide host structure is stabilising the TCNQBr₂ CT salt and TCQF₄ anion radical structures, preventing the photochemical transformations which occur in the monomeric counterparts **4** and **6**.

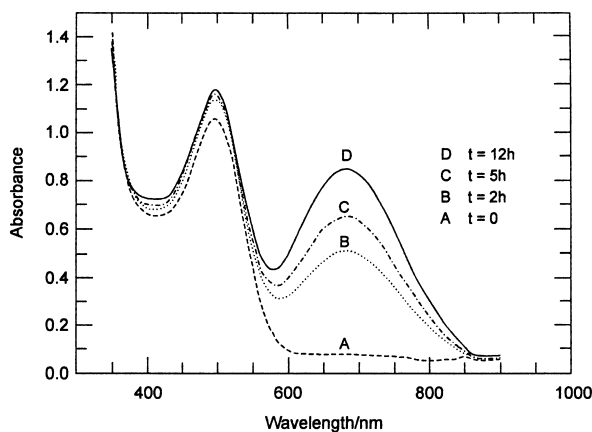


Figure 1. UV-vis spectra of **8**, in DMF solution, before and after photolysis

In summary, new photochromic TCQ chromophores have been synthesised, and incorporated into polymers. These results should encourage further studies on functionalised TCQ systems with the aim of obtaining derivatives suitable for exploitation in optoelectronic devices.

Acknowledgements

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- To a solution of TCNQ **2** (2.5 g, 0.01 mmol) in chlorobenzene was added compound **1** (2.0 g, 0.01 mmol) dropwise and the resulting mixture was refluxed for 24 h, then filtered and the solvents were removed in vacuo to give product **3** (2.0 g, 51%). Purification by chromatography on silica gel using acetone:petroleum ether (bp 40/60) (1:1 v/v) as eluent gave **3** as a red solid, mp 161–164°C; IR (KBr): $\nu_{\max}$ 3446 m (OH), 2159 and 2157 s (CN), 1597 (ArH); UV-vis: $\lambda_{\max}$ (acetone/dichloromethane) 497 nm; ^1H NMR (acetone- d_6): δ 7.82 (2H, d), 7.40–7.28 (4H, m), 6.87 (2H, d), 4.21 (2H, broad, OH), 3.76–3.74 (4H, m), 3.63–3.55 (4H, m); ^{13}C NMR (acetone- d_6): δ 130.9, 129.2, 128.7, 128.0, 113.3, 60.0, 54.8; m/z 358.14288; $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_2$ requires 358.14296. Photolysis in dichloromethane solution afforded **3'** (>95% yield) as a blue solid mp 95–97°C; IR (KBr): $\nu_{\max}$ 3421 m (OH), 2189 and 2123 s

- (CN), 1599 s (ArH); UV-vis: λ_{max} (acetone/dichloromethane) 680 nm; ^1H NMR (CD_3CN): δ 7.70 (4H, s), 7.26 (2H, d), 6.80 (2H, d), 3.67–3.64 (4H, m), 3.55–3.54 (4H, m); ^{13}C NMR (CD_3CN): δ 150.4, 129.9, 128.7, 115.8, 113.4, 59.9, 54.6.
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