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N-Dansyl-carbazoloquinone; a chemical and electrochemical fluorescent switch

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Abstract—A new 'push–pull' molecule having an efficient fluorophore (dansyl) in electronic communication with an active redox quencher (phenyl-carbazoloquinone) through an NH-bridge was designed and synthesized. This all-organic molecule is suggested as a highly reversible 'on/off' molecular switching system. Chemical and electrochemical inter-conversion between the quinone acceptor and the dansyl donor were demonstrated via UV–vis, cyclic voltammetry and fluorescence measurements.

Chemical transducers, or molecular switching systems, find wide interest in science and technology due to their ability to undergo structural changes in response to a respective stimulation. Fluorescent switching device systems find use in probes for the determination of local environmental redox properties and as bio-sensor elements to study electron and energy transfer mechanisms.[1,2] The common molecular switching system has two transformable state systems, resulting in four different integrated configurations or detectable features.[3] Quinones covalently linked to different chromophores and fluorophores represent donor–acceptor systems with reversible redox functions and potential 'switching' properties. In such quinone optical molecular switches, the interconversion of the four distinct states is caused by multiplication of two electrochromic redox states, namely quinone and hydroquinone.[4] This quinone/hydroquinone redox couple can interconvert reversibly by exchanging two protons and two electrons, thus it can serve as the 'antenna' or 'control' subunit, which affects absorption or emission optical properties. Covalent linking of quinones to strong fluorophores results in efficient quenching of the donor emissive state via intramolecular electron transfer from the excited fluorophore to the adjacent quinone acceptor, or by transfer of excitation energy to a low-lying non-emissive charge-transfer state.

Known molecular fluorescent switching systems, operating via a redox couple, consist of a metal-centered redox couple ($M^{(n+1)+}/M^{n+}$)[5,6] or a luminescent ion core[7] (e.g., $[Ru^{II}(bpy)_3]^{2+}$) encircled by a macrocyclic receptor[8] (e.g., an azacyclam metal complex). In this last system, the azacyclam metal complex represents the redox center, connected to a dansyl fluorophore.[8] The mode of linking (spacer) between the fluorophore and the redox sub-unit varies. It can be a direct link (e.g., via a tertiary nitrogen or a methylenic group in the case of the azacyclam ring),[9] it can be an NH group bridging between a quinone and a stilbenic fluorophore,[10] or it can be a non-conjugated spacer (e.g., ethylenic group) connecting a luminescent ion core to a quinone.[7]

In a previous paper, we described the synthesis and both the chemo and electrophotoswitching capabilities of a novel three-component 'all-organic' redox molecular switch.[11] This novel switch was composed of 2-chloronaphthoquinone covalently bridged to 5-dimethylaminonaphthalene (dansyl) via a non-conjugated piperazine spacer. The aim of the present study is to investigate another member of the same motif but with a rigid structure and a conjugated spacer and to learn how these structural changes will influence its switching photochemical properties.

The new molecular switch consists of a rigid and planar carbazoloquinone moiety, covalently bridged to 5-dimethylaminonaphthalene (the fluorophore) via a

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simple NH spacer. This molecular switch (**1**) was prepared in five steps (Scheme 1). In a Michael-like addition reaction, *p*-phenylenediamine (16 mM) was reacted with 1,4-naphthoquinone (8 mM) to yield 2-(4-aminophenylamino)-1,4-naphthoquinone. Reaction with excess acetic anhydride under the catalysis of sulfuric acid[12] gave the acylated product, *N*-4-(3,8-dioxonaphthalene-1,4-dienylamino)-acetamide. Cyclization with $Pd(OAc)_2$ in acetic acid[13,14] afforded the condensed system, *N*-2-(6,11-dioxonaphthalene-5*H*-benzo[*b*]carbazol)-acetamide, which was deacetylated to the 2-amino-5*H*-benzo[*b*]carbazole-6,11-dione. The final step involved reaction with dansyl chloride in the presence of DMAP to give the molecular switch, *N*-2-(6,11-dioxonaphthalene-5*H*-benzo[*b*]carbazole)-5-dimethylaminonaphthalen-sulfonamide **1**.

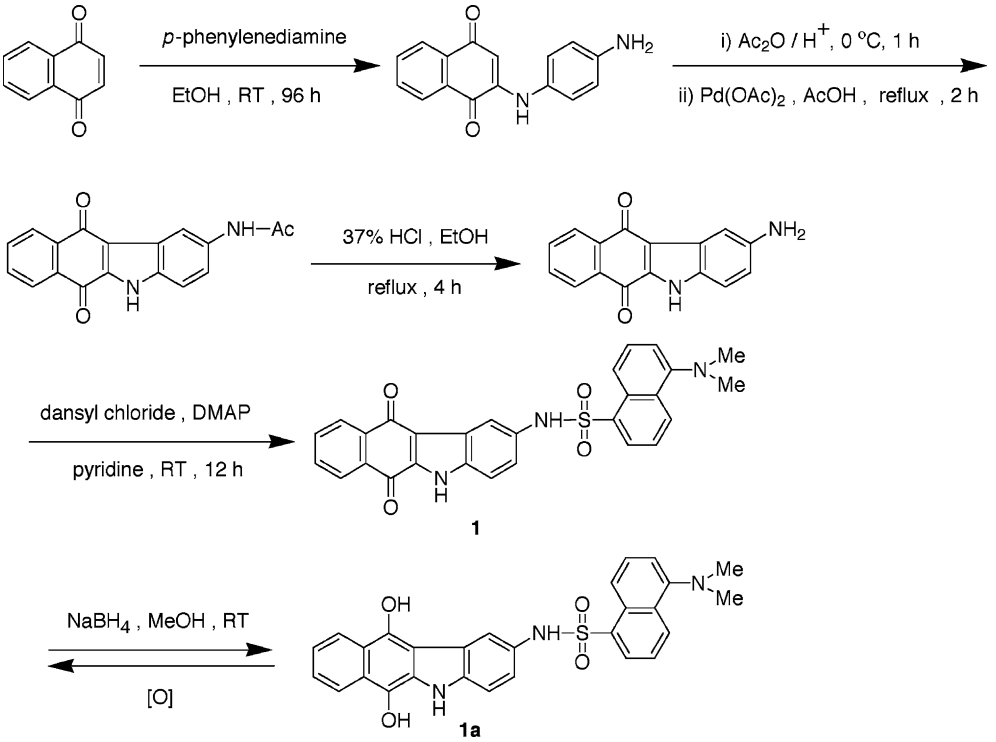
The structure of this new molecular switch was derived from its ^1H and ^{13}C NMR, DEPT and HRMS data.[15] In the ^{13}C spectrum of **1**, the two typical quinone carbonyl resonances were observed at 178.5 and 180.5 ppm, all the aromatics between 112 and 152 ppm and the dimethylamino signal at 45.5 ppm. In the ^1H spectrum, no quinone protons (usually between 5 and 6 ppm) were observed and all the aromatics appeared between 7.1 and 8.6 ppm. HRMS gave the *m*/*z* at 495.125278 proving thereby the composition and structure of **1**.

The structure of compound **1** was firmly established by X-ray crystal analysis (Fig. 1).[16]

As can be seen in the ORTEP diagram, the dansyl and carbazoloquinone ring systems do not reside on the same molecular plane. The torsion angles S1–N1–C1–C2 and N1–S1–C17–C18 between the *p*-phenylenediamine sub-system and the 5-dimethylaminonaphthalene are 130.6° and 93.4°, respectively. The naphthoquinone rings in the stack are parallel and related by an inversion center. The distance between two such rings, as measured between corresponding pairs of atoms, is 4.04 (3) Å. Intermolecular hydrogen bonds are formed between the carbazolic NH of one molecule with the quinone oxygen of a neighboring molecule (2.08 and 2.07 Å), forming centrosymmetric $R_2^2(10)$ hydrogen bond rings (Fig. 1, right). Thus each of the anti-parallel pairs of molecules in the stack is involved in three such bonds.

The UV–vis spectrum (Fig. 2, left) of **1** shows four typical π–π^* aromatic and amino-substituted quinonoid absorptions as expected for such a molecule.[17] The absorption at 400 nm is attributed to intramolecular charge transfer. Indeed, the reduction of quinone **1** to its hydroquinone form **1a** (3×10^{-3} M methanolic solution of $NaBH_4$, reacting with 3.43×10^{-5} M of **1**) is followed by a complete disappearance of the absorption at 400 nm. This transformation is visible as the solution changes from yellow to colorless. A blue shift from 340 nm to a more intense absorbance at 336 nm was also observed. The process is reversible and unless kept under nitrogen, reoxidation occurs within 15 min at room temperature. Reversibility between the quinone and hydroquinone is almost 100% as was detected in the UV absorptions (Fig. 2, left).

The intrinsic fluorescence emission of the dansyl excited state is totally quenched (OFF) in molecule **1**, probably



Scheme 1. Synthesis of molecular switch **1**.

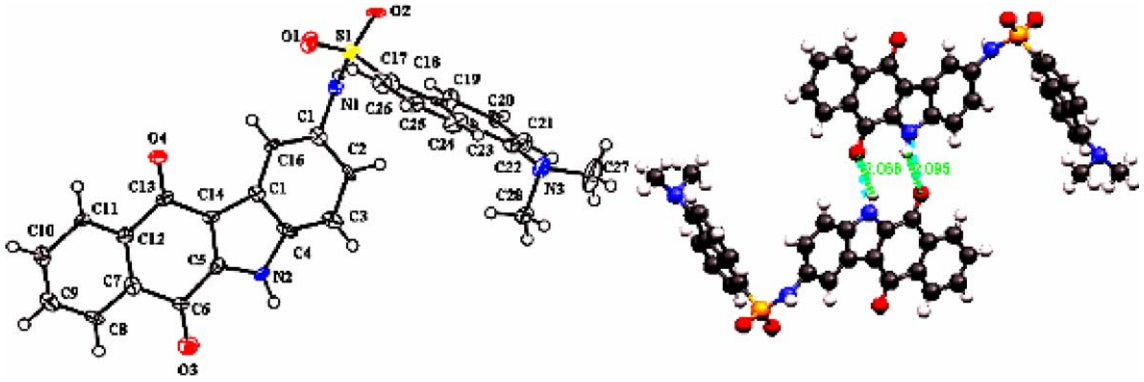


Figure 1. Crystal structure (left) and stacking mode (right) of the molecular switch **1**.

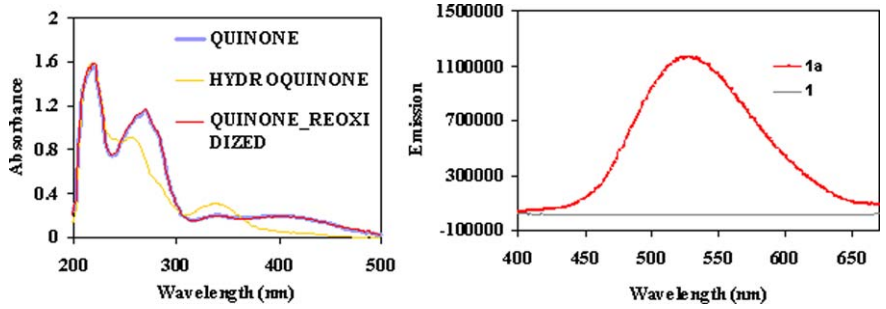


Figure 2. UV–vis absorption of **1** and its reduced form (hydroquinone) **1a** in methanol (left). Fluorescence emission of compounds **1** and **1a** in methanol (right). Excitation 336 nm; emission 528 nm; quantum yield 0.018; Stokes shift 10,822 cm^{-1} [measured using quinine sulfate in 0.1 M H_2SO_4 as a standard].

due to collisionless intramolecular electron transfer from the excited dansyl to the adjacent carbazoloquinone acceptor. However, instant chemical 'ON' fluorescence occurs upon reduction of the quinone with sodium borohydride (Fig. 2, right). Fluorescence quenching of **1** is not solvent dependant, it is fully quenched in protic as well as aprotic polar solvents such as DMSO, ethanol, methanol or acetonitrile/water. This result is in contrast to the behavior of our previous non-conjugated switch[11] where quenching is incomplete in alcoholic medium and some emission is still observed even when the compound is in its quinone form. The emission quantum yield of **1a** is rather modest compared to that of our former model (0.018 and 0.40, respectively), while the Stokes shifts are longer (10822 and 8640, respectively). The differences might be due to the mode of conjugation[18] existing between the excited fluorophore and the rigid carbazolohydroquinone moiety, which are separated by only an NH spacer.

The reduction of quinones is a reversible process, which can be induced both chemically (using reducing agents like $NaBH_4$) and electrochemically (using applied potential). Cyclic voltammetric measurements of **1** were performed in acetonitrile/water (98:2) (Fig. 3) and two one electron reversible processes were observed. The first reversible reduction wave ($E^1_{1/2} = -0.68$ V vs Ag/AgCl) represents the addition of one electron to the quinone moiety (Q) to form a semiquinone anion radical ($Q^{\bullet -}$). The second reversible reduction wave

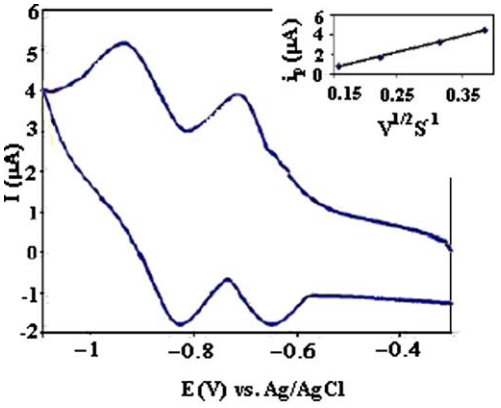


Figure 3. Cyclic voltammogram of **1** in 0.1 M $TBAPF_6$ under an Ar atmosphere, in acetonitrile–water (98:2) performed on a glassy carbon electrode, with ferrocene–Ag/AgCl as a reference electrode.

($E^2_{1/2} = -0.87$ V vs Ag/AgCl) corresponds to the subsequent addition of a second electron to the semiquinone anion radical, producing a hydroquinone dianion (Q^{2-}).[19] Scan rate studies show a linear correlation of I (μA) vs (scan rate)$^{1/2}$ (Fig. 3, inset), indicating diffusion controlled processes for both electrochemical redox steps.

Preparative electrolysis of compound **1** (3.03×10^{-5} M) followed by UV–vis measurements was conducted by applying potentials of −0.6 and −1.0 V (vs Ag/AgCl), respectively (slightly 'more' cathodic than the peaks

corresponding to the reduction of quinone and semiquinone radical anions, respectively). It was found that the redox reaction was accompanied by changes in the UV–vis spectra, demonstrating the electro-interconversion of **1** to **1a** as well as in the opposite direction (95–100%) (Fig. 3).

In conclusion, a new 'all-organic' fluorescent switch was designed and synthesized. In such a system, the redox control, the spacer and the fluorophore subunits can be changed at will to form a variety of new molecular switching systems. Consequently, the emission and the absorption properties can be manipulated and controlled. The synthesis of such donor–acceptor dyads with switchable function exhibiting a 'logic' behavior is of great interest for applications in the field of molecular electronics and molecular recognition. In this letter, we have shown that changing the nature of the spacer from a cyclic non-conjugated to a rigid conjugated structure induces conformational changes that have direct repercussion on the electronic absorption and emission as well as on the switching characteristics.

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15. **1**: mp 211–212 °C. ^{1}H NMR (DMSO, 500 MHz): δ 10.80 (br s, 1H, NH), δ 8.42–8.44 (d, 1H, $J = 9.0$ Hz), 8.38–8.40 (d, 1H, $J = 8.5$ Hz), 8.18–8.20 (dd, 1H, $J = 7.5$, 1.1 Hz), 8.02–8.06 (dt, 2H, $J = 9.0$, 1.3 Hz), 7.87 (d, 1H, $J = 2.1$ Hz), 7.75–7.83 (dsxt, 2H, $J = 9.0$, 8.5, 1.7, 1.3 Hz), 7.61–7.64 (t, 1H, $J = 8.5$ Hz), 7.53–7.57 (t, 1H, $J = 8.5$ Hz), 7.37–7.39 (d, 1H, $J = 9.0$ Hz), 7.23–7.24 (d, 1H, $J = 7.3$ Hz), 7.17–7.19 (dd, 1H, $J = 9.0$, 2.1 Hz), 2.76 (s, 6H). ^{13}C NMR (DMSO, 125 MHz): δ 180.5 (C=O), 178.5 (C=O), 153.0, 138.0, 135.5, 135.2, 134.7, 134.6, 133.6, 133.0, 130.5, 130.2, 129.5, 129.4, 128.6, 126.5, 126.4, 124.6, 123.9, 121.2, 119.2, 117.4, 115.7, 115.0, 112.5, 45.5. DEPT ^{13}C NMR (DMSO, 125 MHz): 134.6, 133.6, 130.4, 130.1, 128.6, 126.5, 126.4, 123.9, 121.2, 119.1, 115.7, 114.9, 112.5, 45.5. HRMS (CI) (m/z): 495.125395 (M^{+}), calcd mass 495.125278 for $C_{28}H_{21}N_3O_4S$.
16. $C_{28}H_{21}N_3O_4S$, orthorhombic, space group Pca21; $a = 20.657$ (3) Å, $b = 7.151$ (9) Å, $c = 30.870$ (13) Å, $V = 4560.1$ (6) Å^3, $Z = 8$, $d = 1.444$ g × cm^{-3}, $T = 120$ (2) K. Diffractometer scan mode: Nonius Kappa CCD, monochromatized Mo-Kα radiation, 2436 unique reflections in the range $2.79 \leqslant 2\theta \leqslant 20.81°$. Full matrix least squares refinement with 2436 reflections [$I > 2\sigma(I)$] and 209 variables; $R = 0.0584$, $R_W = 0.1101$; residual electron density 0.251 e × Å^{-3}. Crystallographic data (excluding structure factors) for the structure in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 292197. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 33603 or e-mail: deposit@ccdc.cam.ac.uk]. Each request should be accompanied by the complete citation of this publication.
17. Electronic absorption data in methanol, for **1**: λ_{max} (nm): 218, 270, 340, 400. Molar absorptivity log ε: 4.46, 4.32, 3.55, 3.54, respectively, and for **1a**: λ_{max} (nm): 216, 256, 336, log ε: 4.46, 4.22, 3.74, respectively.
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