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Diaminodicyanoquinone – A Novel Class of Fluorescent Electron Acceptor Dyes with High Dipole Moments

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Dedicated to Professor Hans-Ulrich Reißig on the occasion of his 70th birthday

Abstract: Fluorescent dyes are applied in various fields of research, including solar cells, light emitting devices and reporters for assays and bioimaging studies. An additional high dipole moment paves the road to nonlinear optics and polarity sensitivity. Redox activity allows switch the molecule's photophysical to properties. Diaminodicyanoquinone derivatives possess high dipole moments, yet only low fluorescence quantum yields, and have therefore been neglected as fluorescent dyes. Here we investigate the fluorescence properties of diaminodicyanoquinones using a combined theoretical and experimental approach and derive molecules with a fluorescence quantum yield exceeding 90%. The diaminodicyanoquinone core moiety provides chemical versatility and can be integrated into novel molecular architectures with unique photophysical features.

Applications of fluorescent dyes range from light harvesting, in solar cells,^[1] light emitting devices,^[2] reporters for the life sciences,^[3] molecular switches^[4] and non-linear optics.^[4-5] 7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a strong electron acceptor used in conductive donor-acceptor systems like TCNQ-tetrathiafulvalene compounds.^[6] An interesting sub-class are diamino-substituted TCNQ derivatives, namely diamino-dicyanoquinones (DADQs), that possess electron donating and accepting moieties linked by a π -system resulting in high dipole moments of 10–20 Debye.^[7] DADQ derivatives have been discussed as novel materials, e.g. for applications in non-linear optics.^[7a] However, their fluorescence quantum yields (QY) in solutions are generally below 0.5% due to non-radiative relaxations of the excited state on the ps timescale.^[8] Only in the solid state, DADQs are moderately emissive with QY of up to

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45%.^[9] Consequently, DADQ derivatives are not considered as fluorescent dyes. Conformational relaxations can have a high impact on fluorescence,^[10] as exploited e.g. for aggregation-induced emission,^[11] where blocking these pathways is used to generate a signal amplification or used as sensing principle for viscosity^[12] and temperature responsive molecules.^[10b, 13]



Figure 1: A) Synthetic route starting with the activation of TCNQ by reaction with pyrrolidine and subsequent reaction with the respective diamine (shown ethylene diamine) to yield compounds **1–7.** B) Chemical structures of **1–4.** C) Photograph of **3** (left) and **4** (right) under illumination with 366 nm light with the respective fluorescence quantum yields in DMSO. Right side: schematics of the mesomeric forms of **4**. The dihedral angles are referred to as D_α and D_β.

Here we demonstrate substitution pattern control of QY in DADQs, with QY exceeding 90% (see **Figure 1**). Theoretical calculations reveal that benzene functionalized DADQs show high QY as their molecular structures remain close to the ground state conformation after photoexcitation without being submitted to internal conversion (IC) or intersystem-crossing (ISC). Accordingly, DADQ derivatives may now be considered as fluorescent dyes and thus applications, such as optical switches or non-linear optics are coming into reach.

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Results and Discussion

At first 7,7-diamino-8,8-dicyanoquinomethan (TCNQ) was reacted with pyrrolidine to activate the substitution of the geminal cyano groups of TCNQ in the 7,7 position.^[14] This 7-pyrrolidino-7,8,8-tricyano quinomethane (PTCNQ) reacts with the respective amine to compounds **1–4** (**Figure 1A**) in 40–80% yields. The compounds were characterized by ¹H and ¹³C NMR, FTIR, EA and MS. In addition, the absorption and fluorescence properties were investigated in selected solvents.



Figure 2: Absorption (black) and fluorescence spectra (blue) of 3 (dashed) and 4 (solid) in acetonitrile (normalized with respect to the fluorescence of 4). The vertical orange bars represent transitions of compound 3 (349 nm, oscillator strength: 1.02 a.u.) and 4 (363 nm, oscillator strength: 1.30 a.u.) calculated using TD-DFT at the CAM-B3LYP level. Insets: Difference densities between ground state and excited state of 4 (left) and 3 (right) to visualize the electron flow during the electronic excitation. Blue and red areas correspond to areas of electron enhancement and depletion, respectively. Isovalue = 0.005 Å⁻³.

The molar absorption coefficients are solvent dependent and reach values of up to $58,000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ in acetonitrile (ACN) as depicted in **Figure 2** for **4**. While the unstructured absorption band lies between 300 and 400 nm, the fluorescence is shifted bathochromically by 40-90 nm (25×10^4 - $11.1 \times 10^4 \text{ cm}^{-1}$).

The difference densities between ground state and excited state (inset Figure 2) illustrate the shift in electron density from the dicyanomethane to the amine groups upon photoexcitation. This transition leads to a notable reduction of the dipole moment in the excited state from approximately 30 D to 22 D (Table S9), well known for DADQs, and is the reason for the observed negative solvatochromism (Figure S2 and Table S2).[15] In addition, the So- S_1 transition in 4 is extended across the enlarged π -system, including the phenyl ring. The, absolutely measured, QY values are summarized in Table 1. Compound 4 shows very high QY in all solvents, with values of 92% in dimethyl sulfoxide, (Figure 1C) around 70% in tetrahydrofuran, dimethylformamide and acetonitrile and 56% and 35% in ethanol and methanol, respectively. In contrast, 1 and 3 show QY in the range of 0-12% and 2 QY of < 1%. The fluorescence lifetimes of 1-4 and the calculated radiative and non-radiative rate constants (Table S3/S4) do not show a straightforward correlation with the QY data. QY measurements in solvents of varying viscosity confirm the assumption that rotations around the dihedral angles D_{α} and D_{β} play a significant role for the non-radiative excited state

deactivation of 1–3. By increasing the fraction of polyethylene glycol (PEG) in ethanol (PEG-EtOH) from 0% to 75%, we observe a 3 – 7-fold increase in fluorescence intensity for 1–3 (Figure 3 and Figure S7), resulting in an increase of QY of 2 from 0.4% to 2.9%. In contrast, the fluorescence of 4 is barely affected by an increase in solvent viscosity (Figure S7D).



Figure 3: Absorption spectrum and emission spectra of 3 in EtOH-PEG mixtures ranging from 0 to 75% PEG in steps of 25%, depicted by the red arrow. Solid 0%, dash 25%, dot 50%, dash-dot 75%. With an increasing ratio of PEG and hence increasing viscosity, the fluorescence intensity increases by a factor of 3.3.

For compounds 1–4 the fluorescence intensity decreases by more than 30% with increasing temperature in the temperature range of 40 °C to 110 °C (Figure S9). Upon decreasing the temperature (273 K–173 K), the fluorescence intensity increases qualitatively for 1–4 (Figure S11). A closer look at the shape of the fluorescence signals indicates that various fluorescent states are populated (Figure S12). As viscosity effects and aggregation upon these temperature changes are not thoroughly studied, the observed trends are qualitative.

The experimental results indicate that rotations play a major role to control the QY. In particular, the N-substituted derivatives **2** and **7** (Figure 1 and 4), twisted in their ground state structure at D_{α} (Figure S17C), are non-fluorescent. In analogy to 4, compounds **5** (Br-derivative) and **6** (CN-derivative), both sharing the benzene unit, are highly fluorescent (Figure 4 and Table 1).



Figure 4: Chemical structure of compounds 4–7 with symbolic pictures of their fluorescence.

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| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------------|---------|-------|-------|------|-------|-------|-------|-------|
| Εт ^N | Solvent | Φ [%] | Φ [%] | Φ[%] | Φ [%] | Φ [%] | Φ [%] | Φ [%] |
| 0.207 | THF | 7 | < 1 | 7 | 73 | 34 | 69 | < 1 |
| 0.386 | DMF | 7 | < 1 | 10 | 72 | 62 | 81 | 3 |
| 0.444 | DMSO | 10 | < 1 | 7 | 92 | 39 | 90 | < 1 |
| 0.460 | ACN | 7 | < 1 | 12 | 71 | 18 | 53 | < 1 |
| 0.654 | EtOH | < 1 | < 1 | < 1 | 56 | 63 | 70 | < 1 |
| 0.762 | MeOH | < 1 | < 1 | < 1 | 35 | 20 | 30 | < 1 |

Table 1: Fluorescence quantum yields of compounds 1–7 in solvents of different polarity. Values for the normalized Dimroth-Reichardt Parameter E_T^N were taken from Ref. ^[16]

Theoretical Investigation

To gain more insight into the optical properties of our DADQ derivatives and to elucidate the remarkable QY of **4**, we performed time-dependent density functional theory (TD-DFT) calculations at the CAM-B3LYP^[17] level for **1–4** and **7** using ACN as the solvent with CPCM (ε = 37.5).^[18]

A prerequisite for a high QY is a close similarity between the relaxed structures of the excited state and the ground state without IC or ISC events influencing the photoexcitation process. The fluorescence deactivation of the DADQ species may be controlled by two photoinduced intramolecular torsions at dihedral angles D_{α} and D_{β} (Figure 5).



Figure 5: Two kinds of intramolecular torsion angles (shown for 2) that affect the fluorescence deactivation mechanism in DADQs: D_{α} (left) and D_{β} (right).

To our surprise, the ground (S_0) and excited state (S_1) structures of all compounds hardly differ (**Figure S16**) along with rather constant oscillator strengths (**Table S8**). As this would imply all compounds show similar QY, a more detailed look at the potential energy surfaces (PES) of the intramolecular rotations is needed. To account for the influence of multireference states we opted for the DFT/MRCI method originally proposed by Grimme and Waletzke^[19] and revised by Marian *et al.*^[20] with a Kohn-Sham orbital basis generated at the CPCM/BHLYP/def2-TZVP^[21] level to obtain accurate energies. Test calculations showed that the

rotational barriers at D_α and D_β do not critically influence each other (Figure S17A/B), which is why we will treat D_{α} and D_{β} separately. In the S₀, rotation around D_{β} at the Franck-Condon point is hindered by large barriers of around 60 kJ/mol for all compounds, but a rotation around D_{α} is possible except for 2 and 7 where the N-substituents block the way (Figure S17C/S18A). In contrast, in the S₁ rotation around D_{α} is prevented with barriers of 60–100 kJ/mol, but rotation around D_β shows barriers of around 12 kJ/mol (1-3) to 25 kJ/mol (4, 7) (Figure S17D/Figure S18B). Large barriers arise as a rotation around D_β diminishes the basis function overlap between the π-orbitals centered at the phenyl ring and those at the nitrile groups in the HOMO, while a rotation around D_{α} decreases the overlap between the phenyl ring's π orbitals and the p-orbitals of the amine groups in the LUMO. Low barriers are explained by nodes present in the HOMO at D_{α} and in the LUMO at D_{β} , where an intramolecular torsion would not impede any orbital overlap (Figure 6).



Figure 6: HOMO (left) and LUMO (right) obtained at the BHLYP/def2-TZVP level. Rotations (indicated by arrows) are favored due to nodal planes in the orbitals, while orbital overlap keeps the structures rigid at D_β in the HOMO (left) and at D_α in the LUMO (right), isovalue = 0.003 Å³.

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Figure 7: PES scan of the S₁ state around dihedral angle D_{β} for 1–4 computed at the CPCM/BHLYP/def2-TZVP/MRCI level. 7 is omitted as its fluorescence deactivation mechanism is different.

The PES at D_{α} is less important for **2**, **3**, and **4**, where an electronic excitation somewhere along the S₀ PES will just recover the S₀ minimum structure on the S₁ PES through relaxation. However, this torsion may account for fluorescence quenching by IC or ISC in **7** and slightly in **1**. For **1–4**, QY loss is expected to mainly occur due to the relatively small rotational barrier in the S₁ at D_β (**Figure 7**). As expected, the respective rotational barrier is highest for **4** and lowest for **1**. This can be attributed to the stabilization of the ground state geometry of **4** through the extended π -system. Using Arrhenius' equation at T = 300 K, we define k_{rot} ⁻¹ (the reciprocal rate constant for the rotation around D_β, (**Equation S5**)) as a relative measure to compare rotational barriers. Relating k_{rot} ⁻¹ for **1–4** illustrates that **4** is up to 480 times more likely to fluoresce after photoexcitation into the S₁ than **1-3**:

k_{rot}^{-1} (1): k_{rot}^{-1} (2): k_{rot}^{-1} (3): k_{rot}^{-1} (4) = 1: 3: 12: 481.

ISC events between singlet and triplet surfaces contribute to fluorescence quenching in all compounds. For **7** the most likely deactivation mechanism is via an ISC of the S₁ with T₁ and T₂ along D_α (**Figure S19A**). This mechanism may play a role for **1** as well, however, it is assumed to have a smaller impact (**Figure S19B**). At D_β all compounds show a singlet/triplet separation energy of around 0.7 eV at the Franck-Condon point, which should be just large enough to prevent ISC events. However, as the S₁ and the T₀ eventually come very close at an angle of around 90° (**Figure S20**) in all molecules, the rotational barrier presented by k_{rot}⁻¹ and the non-radiative relaxation through ISC events are directly linked. Since **1–3** are much more likely to overcome the rotational barrier at D_β than **4**, their QY is significantly lower.

While this qualitatively accounts for the drastic differences in QY, it does not fully explain the large QY of **4** by itself. As solvent effects have only been included in an implicit way, an explicit solvent cavity of ACN was set up (**Figure S21A**) and the rotational barrier at D_{β} was recalculated for **1** and **4** with the smaller def2-

SVP basis set and fixed solvent molecules to save computational resources (**Figure S21B**). While the total barrier hardly changed for **1**, the barrier height for **4** increased by roughly 30%. Thus, the solvent shell may play a significant role at least in the case of **4**, where it likely contributes to its large QY.

To further characterize 1-4, we performed cyclic voltammetry (CV) experiments in a 0.1 M Bu₄NPF₆ solution of DMF (Figure S14). The molecules show a complex redox behaviour, with mostly reversible oxidations (for 4) and irreversible reductions (quasi reversible for 2), which likely involve the proton of the secondary amine and provide a hint for an electron transfer followed by a chemical reaction (EC mechanism).^[22] As expected, the substitution of cyano moieties for secondary and tertiary amines favours oxidation processes, which are not observed for TCNQ (Figure S15). This also renders the molecules more electron-rich and causes a cathodic shift of the reduction potentials. (see Table S7 for more details). The HOMO-LUMO gaps were calculated at the CPCM/BHLYP/MRCI level. The trends between experiment and theory show overall agreement (Table 2). The electrochemically measured gaps differ slightly in absolute values, as the solvent model neglects bulk effects at the electrode.[23]

Table 2: Electrochemical, theoretical, and optical data of Compounds 1-4 with the resulting orbital energies and HOMO–LUMO gaps (E_g) [eV].

| | | Theory ^{c)} | | | |
|---|---------------------------|---------------------------|-------------------------|----------------------------|------------------|
| | | CV data ^[a] | | optical data ^{b)} | |
| | Е _{номо} [eV] | E _{LUMO} [eV] | E ^{el} [eV] | E ^{opt} [eV] | $E_g^{theo}[eV]$ |
| 1 | -2.37 | 0.16 | 2.53 | 3.31 | 3.24 |
| 2 | -2.42 | 0.12 | 2.54 | 2.87 | 3.49 |
| 3 | -2.27 | -0.14 | 2.13 | 3.16 | 3.17 |
| 4 | -2.22 | -0.21 | 2.01 | 2.94 | 2.98 |

[a] Orbital energies calculated from the first reduction or oxidation half-wave potentials referenced to FcH/FcH⁺(-4.80 eV): ϵ = (-(E_{1/2}-4.80) eV [b] The optical HOMO-LUMO gap was determined from the onset at the red edge of the absorption band [c] CPCM/BHLYP/def2-TZVP/MRCI.

Conclusion

We synthesized highly fluorescent diaminodicyanoquinones showing quantum yields of over 90% when benzene substituted. We attribute the high fluorescence quantum yields mainly to restricted internal rotations while quenching occurs through the intersection of singlet and triplet states. However, other effects, such as molecular aggregation, may contribute as well. The electrochemical characterization of these molecules reveals complex redox activity. In summary, we could show that diaminodicyanoquinones derivatives are a novel class of fluorescent dyes customizable for photophysical applications, the potential of which needs to be studied in more detail.

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Keywords: dipole moment • fluorescence • quantum yield • quinone

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Controlling the internal rotation around dihedral angle D_{β} in diaminodicyanoquinones in the excited states, determines the fluorescence quantum yield exceeding 90%.

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