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A highly soluble asymmetric perylene-*bis* (dicarboximide)-acceptor system incorporating a methylene bridged methoxybenzene-donor: solvent dependence of charge transfer interactions

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The synthesis and photophysical properties of an asymmetrically substituted perylene-*bis*(dicarboximide), (PDI), system (**1**) containing a methylene bridged 4-methoxy-benzene donor and a solubilizing branched C₁₃ alkyl chain are described. As compared to most PDIs, the fluorescence of **1** is strongly quenched in polar (but not in non-polar) solvents due to a photo-induced electron transfer process. Transient absorption spectroscopy and time resolved emission in e.g. acetonitrile indicates that upon excitation the radical anion of the PDI is formed with a rate of ca. $3.5 \times 10^9 \text{ s}^{-1}$, and the charge transfer state has a lifetime of ca. 3 ns. A Frontier Molecular Orbital description is provided, by using DFT calculations.

Key Words: Perylene dyes, photoconductivity, solar cells, LED, 3,4,9,10-perylenetetracarboxylic diimide, excited state properties, photoinduced electron transfer, transient absorption, time resolved emission

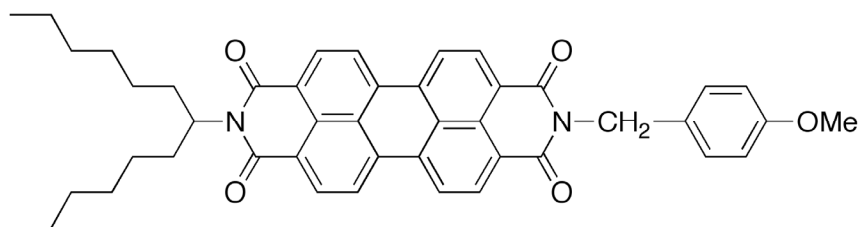
Introduction

Perylene-*bis*(dicarboximides) are extremely stable organic dyes of which the chemistry has been explored in many directions and which have been applied in many fields ranging from car paints, hair-treatment compositions, active conducting components in photocopying devices, to laser dyes.¹ The electron accepting abilities of perylene-*bis*(dicarboximides) (PDIs) make them interesting components for electron transfer systems² and for application in opto-electronic devices. Several examples have been reported where perylene dyes are the

n-type material in organic solar cells.^{3,4} Alkoxybenzene groups as donor units for charge transfer PDIs can be easily incorporated into supramolecular functionality and allow selective perylenebisimide excitation.^{5,6}

The synthesis of asymmetrically substituted PDIs is not trivial and 3 methods are available: via the mono-potassium salt of perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA) in a reaction in water;⁷ by using a reaction of PTCDA with equimolar amounts of 2 similar amines in the standard coupling in imidazole followed by separation of the statistical mixture formed;^{2,8} via a symmetric PDI, followed by hydrolysis with base to the mono-imide-mono-anhydride and subsequent coupling with a second amine.⁹ The first (water based) method was recently described with (S)-(-)-1-phenylethylamine.¹⁰ Using ammonia as the first reagent in the water based method can result in asymmetric PDI systems that can be functionalized further by N-alkylation.¹¹

Here a PDI system containing a 4-methoxybenzene donor and a solubilizing branched C₁₃ alkyl chain is presented and its photophysical properties are investigated. The asymmetric compound is synthesized by the reaction in water of the mono-potassium salt⁷ of the PTCDA with 4-methoxybenzylamine, followed by the standard coupling¹² of the mono-imide-mono-anhydride in imidazole with 1-hexylheptylamine to obtain the asymmetrically substituted PDI **1**.



Scheme 1. The electron donor-acceptor system **1**.

Experimental

Synthesis

Perylene-3,4,9,10-tetracarboxylic acid monoanhydride monopotassium carboxylate (monopotassium salt of PTCDA)

3 g of perylene-3,4,9,10-tetracarboxylic-dianhydride (Aldrich) was mixed with 35 mL of 5% KOH solution (pH = 10.5). At 90 °C, in a period of 3 to 4 h, 12.5 mL of 10% phosphoric acid was added dropwise, until the pH was between 4.5 and 5.5. If a drop is put on filter paper now, there is a dark brown solid that does not migrate, and a colorless solvent that migrates through the paper. (At higher pH, the migrating solvent still contains yellow/green substance). After stirring for 1 h at 90 °C, the monopotassium salt was isolated on a frit filter. If washed with water, material washed through the filter.

Yield: 1.64 g (3.7 mmol); 47% Bordeaux-red amorphous material.

IR(KBr): 1760(s), 1720(s), C=O, anhydride.

N-(4-methoxybenzyl)-3,4,9,10-perylenetetracarboxylic-3,4-anhydride-9,10-imide (Perylene-monoimide-mono-anhydride)

To a mixture of 4.5 mmol (0.48 g, 0.6 ml) 4-methoxybenzylamine in 45 mL of water at 0 to 5 °C was added the monopotassium salt of PTCDA (1.1 mmol, 0.45 g). An immediate color change was observed. The mixture was allowed to react for 4 h without cooling, and was then warmed to 90 °C over 2 h (the formed carboxamide is prone to hydrolysis and should not be left in solution overnight). Then 11.5 mL of 20% phosphoric acid was added. After 2 h, the precipitated product was isolated on a frit filter and washed with water. To remove bisimide and dianhydride the material was treated with 60 mL of 10% KOH for 2 h. The di-potassium salt of the monoimide precipitates. Complete precipitation is accomplished by adding a concentrated KCl solution (salting out). A drop on filter paper should migrate yellowish through the paper, not reddish.

The precipitate is isolated on a frit filter after cooling, and washed with 8 % KCl and 2 % K₂CO₃, until the filtrate is colorless (to remove the tetra-potassium salt of the bis-anhydride). The residue is dissolved in hot water and filtered to remove bisimide. From the filtrate the monoimide-mono-anhydride was isolated at 90 °C by adding acid (HCl). The product was isolated and dried.

Yield: 0.19 g (0.4 mmol); 36% black amorphous material.

IR(KBr): 1765(s), 1730(m), C=O, anhydride; 1690(s), 1650(s), C=O(imide).

As can be read in reference 9d, this method only works with amines that are water soluble. It does not work with e.g. 1-hexylheptylamine.

N-(1-hexylheptyl)-N'-(4-methoxybenzyl)-3,4,9,10-perylenebis(dicarboximide) (Formation of the asymmetric PDI 1)

To 5 g of imidazole and 330 mg (1.66 mmol) hexylheptylamine was added 100 mg (0.196 mmol) of mono-imide-mono-anhydride, and the mixture was heated at 160 °C under N₂ for 4 h.

To the cooled-down mixture were added 100 mL of ethanol and 300 mL of 2 M HCl. This mixture was extracted with dichloromethane, which was then washed with water and NaOH. The solvent was removed. The compound was purified by column chromatography (3 times), using chloroform as eluent, (TLC, CHCl₃, d = 0.25 mm, R_f = 0.2). The material can be crystallized from chloroform-acetone mixtures, or from boiling cyclohexane to which drops of chloroform or acetone are added to dissolve all material and slow cooling to room temperature.

Yield: 100 mg = 0.14 mmol = > 73% shiny reddish-pink material.

The official CAS name of this compound **1** is expected to be:

Anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone, 2-(1-hexylheptyl)-9-[4-methoxyphenyl]methyl].

Spectroscopic data for 1: IR (CHCl₃): 3200(w), 3020(m) C=C; 2950(s), 2920(s), 2850(s), CH; 1650(s), 1690(s) C=O (imide); 1610(w), 1590(m), 1575(w), C=C. ¹H-NMR (CDCl₃, 250 MHz): δ 0.81, t, 6H, J = 6.6 Hz, (Me); 1.22-1.32, 16H, (alkyl); 1.83-1.91, m, 2H, CH₂ CHN; 2.22-2.31, m, 2H, CH'₂ CHN; 3.75, s, 3H, (MeO): 5.14-5.21, tt, 1H, J₁ = 10 Hz, J₂ = 5.8 Hz, (CHN); 5.26, s, 2H, (NCH₂ ph); 6.85, d, 2H, J = 8.6 Hz, (ph) ; 7.53, d, 2H, (ph); 8.28, d, 2H, J₁ = 8 Hz, J₂ = 3.15 Hz, (per); 8.40, dd, 4H, J₁ = 8 Hz, J₂ = 2.3 Hz, (per); 8.58, d (broad), 2H, (per). ¹³C-NMR (CDCl₃, 63 MHz); δ = 4.03, (Me); 22.60, (CH₂); 27.01, (CH₂); 29.25, (CH₂);

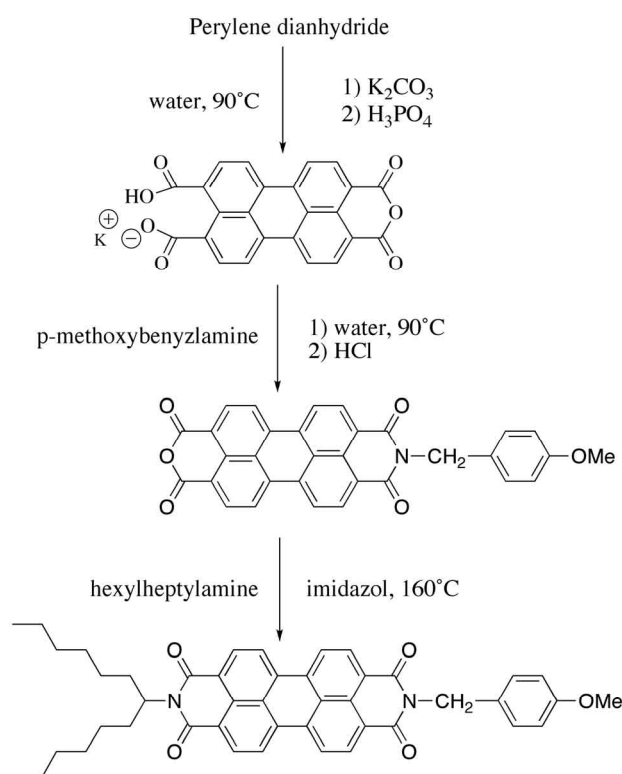
31.78, (CH₂); 32.45, (CH₂); 43.12, (NCH₂ ph); 54.90, (CHN); 55.27, (MeO); 113.85, (ph); 122.69, 122.95 (CH per); 123.04, 126.14, 129.00, 129.41, (C_q per); 130.80, (ph); 131.24, (CH per), 134.04, (C_q per); 134.48, (C_q ph); 159.17, (C_qO ph); 163.09, (CO).

MS FAB⁺ MH⁺ 693.3328 (calcd); 693.3313 (obsd). ϵ of **1** is 87700 M⁻¹cm⁻¹ at 528 nm in CHCl₃

NMR Double-resonance: When irradiated at 5.19 ppm, the signals at 1.9 and 2.25 ppm change from multiplets to 2 triplets. The CH₂CHN and CH₂'CHN protons have a different chemical environment due to the presence of the carbonyl groups.

Melting point: (red needles from cyclohexane-acetone): 312.8-313.5 °C

Purity was checked by HPLC (reversed phase, C₁₈ column, acetonitrile as eluent, flow = 1 ml/min, P = 20 Mpa, Rt = 2.7 min), which indicated 99.9% purity.



Scheme 2. Synthetic route to charge transfer PDI system **1**.

Details on the spectroscopic methods (SPC and transient absorption spectroscopy) are reported elsewhere.¹³ Emission quantum yields were determined with the “optical dilute relative” method¹⁴ on a SPEX Fluorolog, using Rhodamine 101 in ethanol as a reference.¹⁵

For the spectroscopy, heating with a hot-air pistol was used to prepare the solutions (when needed) and filtration over a cotton plug was applied to remove particles.

Molecular modeling was performed with the Spartan'04 V1.03 package (Wavefunction Inc.) The equilibrium geometry in the ground state was calculated using Density Functional B3LYP with 6-31G. Orbitals were visualized at 0.01 electrons/au³.

Results and discussion

The shape of the absorption and emission spectra of **1** are very common (see Figure 1) and the UV-Vis absorption spectrum of **1** is only slightly solvent dependent and shows 3 characteristic (average) maxima around 455, 486, and 522 nm ($\pi \rightarrow \pi^*$ transitions) and a shoulder at ~ 430 nm. As compared to most PDIs,¹⁶ however, the fluorescence of **1** (with maxima average around 530, 570, and 620 nm) is strongly quenched in polar solvents. Representative UV-Vis absorption spectra in cyclohexane (with maxima at 517, 481, 451, 260, and 220 nm) and ethylacetate (with maxima at 520, 484, 454, and 260 nm) are given in Figure 1.

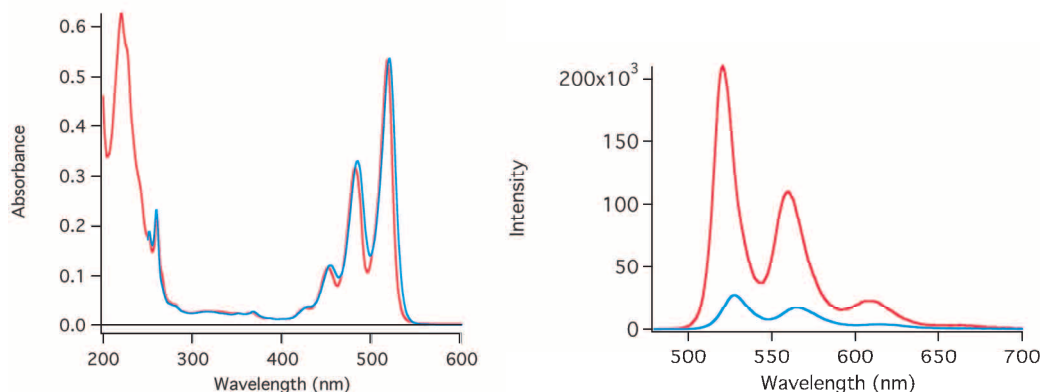


Figure 1. UV-Vis absorption spectra (left) together with emission spectra (right) of **1** in cyclohexane (red) and in ethylacetate (blue).

Emission maxima observed are 521, 559, and 609 nm in cyclohexane and 527, 565, and 616 nm in ethylacetate. It is interesting that the fluorescence quantum yields range from unity in n-hexane, to only a few percent in acetonitrile. Clearly a very strong solvent effect is occurring, in which the polarity of the solvents is of major importance. We attribute this quenching to a photoinduced electron transfer process. Emissive properties of **1** are given in Tables 1 and 2.

Table 1. Solvent dependence of the fluorescence quantum yield (Φ_f), together with the Δf value of the solvents.

Solvent	Δf	Φ_f
n-hexane	0.092	0.99
Cyclohexane	0.100	0.73
Toluene	0.126	0.67
Dibutylether	0.194	0.42
Chloroform	0.251	0.14
Ethylacetate	0.292	0.10
Dichloromethane	0.319	0.09
Acetonitrile	0.393	0.07

Δf is the solvent polarity parameter.

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)$$

The rate with which this quenching process occurs can be inferred from time resolved emission measurements. The fluorescence lifetimes as obtained with single photon counting of **1** in various solvents are given in Table 2. As in the steady state measurements, a clear solvent effect is present and the lifetime becomes shorter in more polar solvents.

Table 2. Solvent dependence of the fluorescence lifetime (τ_f with χ^2) and derived rate of electron transfer (k_{cs}), together with the dielectric constants (ϵ) of the solvents.

solvent	ϵ	τ_f (ps)	χ^2	k_{cs} (s^{-1})
n-hexane	1.88	3450	1.10	0
c-hexane	2.34	3300	1.05	1.3×10^7
ethylacetate	6.02	340	1.12	2.6×10^9
acetonitrile	37.5	262	1.2	3.5×10^9

A direct proof of charge separation is the fact that in polar solvents the radical anion of the PDI moiety can be observed with transient absorption spectroscopy. In the transient absorption spectra the clear features of the radical anion of the PDI are observed, with maxima at 700 and 840 nm.^{6,17} Also localized at around 700 nm is the $S_1 - S_n$ absorption of the PDI unit; however, its lifetime is only 340 ps (see Table 2) and is therefore not clearly distinguished. Furthermore, some emission can be observed around 620 nm, as a negative signal. Transient absorption spectroscopy and single photon counting of **1** in acetonitrile thus indicates that upon excitation the radical anion of the perylenebisimide^{6,17} is formed with a rate of $\sim 3.5 \times 10^9 s^{-1}$, and the charge transfer state has a lifetime of ca. 3 ns (see Figures 2 and 3). The charge separation rates (k_{cs}) were calculated with the following equation in which the lifetime in n-hexane was taken as τ_{ref} . This lifetime is similar to that of other strongly emissive perylene *bis*(dicarboximides).¹⁶

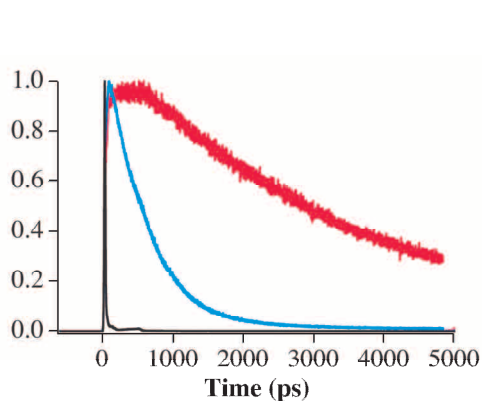


Figure 2. Time resolved emission of the electron donor acceptor system **1** in n-hexane (long lived in red) and ethylacetate (short lived in blue). Laser pulse is also shown (in black) ($\lambda_{ex} = 324$ nm, FWHM = 19 ps, $\lambda_{det} = 570$ nm).

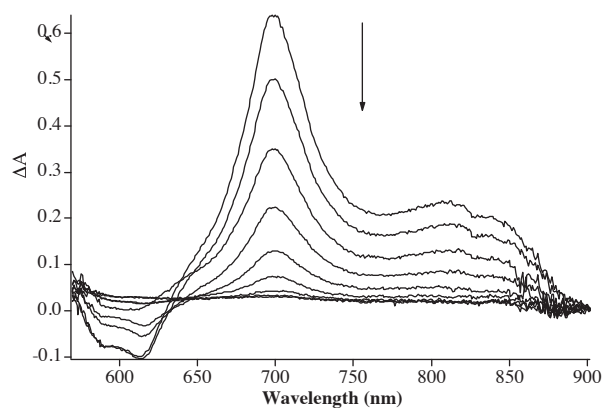


Figure 3. Transient absorption spectra of the electron donor acceptor system **1** in ethylacetate ($\lambda_{ex} = 480$ nm, incremental time delay is 1 ns).

$$k_{cs} = 1/\tau_f - 1/\tau_{ref}$$

Clearly, even with a moderately strong donor, such as methoxybenzene, in polar solvents fast photoinduced charge transfer occurs in the system, resulting in a highly polar state that has a reasonable lifetime. Stronger electron donors could be applied to achieve electron transfer interaction in non-polar media. The asymmetry allows solubilization and determination of the charge transfer properties in many different solvents, which will enable the design of new and improved functional molecules as e.g. photoconductors, components in molecular switches or sensors.

Photo-excitation of this simple methoxybenzyl substituted perylene dye gives fast ($3.5 \times 10^9 \text{ s}^{-1}$) photoinduced intramolecular electron transfer, resulting in a dipolar state of which the perylenebisimide radical anion can be observed for a few nanoseconds.

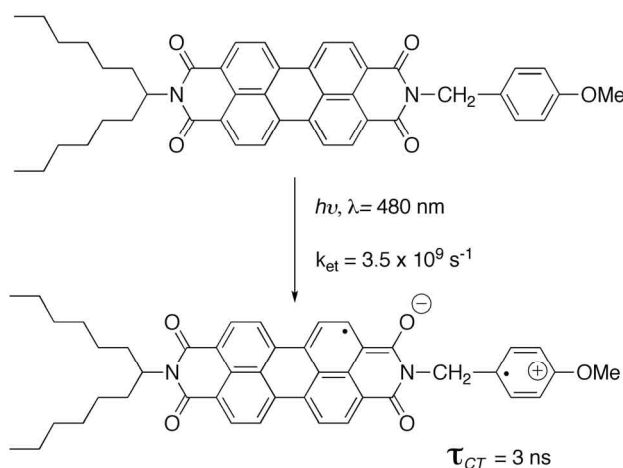


Figure 4. Representation of the photoinduced process occurring in compound **1** leading to the formation of a charge transfer state consisting of the radical anion of the acceptor and the radical cation of the donor.

By using the appropriate data we can estimate¹⁸ the Gibbs energy of photoinduced electron transfer: ($E^0(\text{D}^{\cdot+}/\text{D})$ is estimated^{19,16} to be +1.4 V vs SCE, $E^0(\text{A}/\text{A}^{\cdot-})$ is estimated¹⁷ to be -0.73 V vs SCE and ${}^1\Delta E_{0,0}$ is 2.31 eV. From these data we can expect that there is a negative $\Delta_{\text{ET}}G^0$ in polar solvents of ca. -0.18 eV. From the fluorescence data it is clear that in the non-polar solvent n-hexane the charge transfer interaction is not occurring.

Molecular Orbital description

From the experimental data it is clear that in compound **1** a photoinduced electron transfer interaction is occurring in polar solvents. A simple frontier molecular orbital (FMO) description of this process in a Donor/Acceptor (D/A) system, in which the acceptor has the lowest excited state, is given in Figure 5.

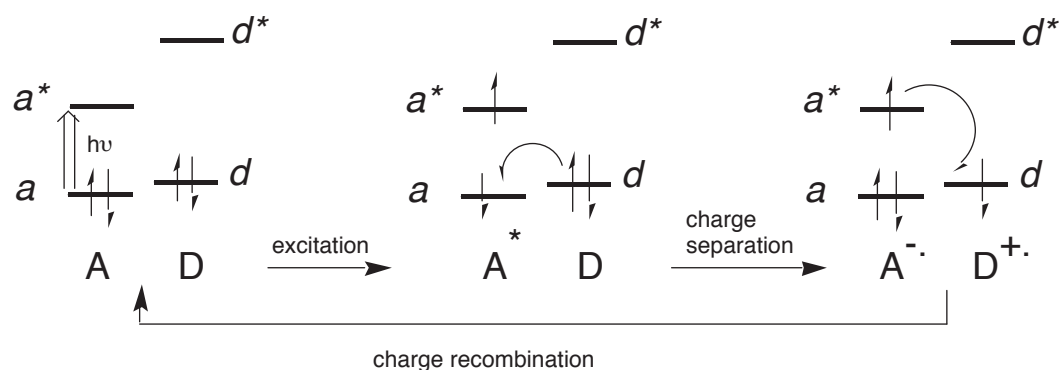


Figure 5. FMO representation of charge separation and charge recombination following local excitation of the acceptor in a D/A system.

The HOMOs and LUMOs of D and A are labeled d , d^* and a , a^* , respectively. Local acceptor excitation ($a \rightarrow a^*$) is followed by electron transfer involving orbital interactions between d and a , while charge recombination involves interactions between a^* and d . The FMO description is undoubtedly an oversimplification, which may, for example, neglect important interactions between charge-transfer configurations and locally excited configurations.²¹ Nevertheless, it is a useful starting point²¹ for identifying important orbital interactions. The obtained structure as well as the MOs of the full molecular system **1** is shown in Figure 6, as obtained from DFT calculations using SPARTAN (Wavefunction Inc). Since donor and acceptor are incorporated in one molecule this implies: a (= HOMO-1), a^* (= LUMO) and d (= HOMO). It is interesting that in this system the PDI orbitals are rather un-perturbed.^{22,23} Furthermore, it can be seen that the HOMO located on the methoxybenzene unit is slightly delocalized via the bridging CH_2 group to the nitrogen atom of the imide.

It is interesting that the energy difference between the HOMO-1 and the LUMO (2.53 eV) relates rather well to the ${}^1\Delta E_{0,0}$, that is 2.31 eV. The experimental results, together with DFT MO calculations, indicate that the special properties of system **1** allow fast photoinduced charge separation.

Conclusions

By incorporating a methoxybenzene substituent with a methylene spacer onto the PDI nitrogen we drastically change the properties in a polar environment, relative to e.g. alkyl substituted systems. Charge transfer interactions between the donor unit (methoxybenzene) and the acceptor unit (perylene-*bis*(dicarboximide)) are clearly present. Charge transfer occurs on the $\sim 3 \times 10^9 \text{ s}^{-1}$ scale and charge recombination is ca. 10 times slower ($3.3 \times 10^8 \text{ s}^{-1}$). The asymmetric electron donor acceptor system was synthesized using the water-based method starting from the mono-potassium salt of the PTCDA. DFT calculations are in agreement with these experimental observations and give insight into the orbitals involved in the charge separation process. This work could be used for a better design of molecular components in photoconductors and other opto-electronic devices. Furthermore, charge transfer PDI **1** can be considered as a fluorescence-intensity probe-molecule that is sensitive towards dielectric or electric field effects, that can occur in transmembrane potentials²⁴ or for probing polymer

rheology and glass transitions.²⁵ Asymmetrically substituted perylene-bis-(dicarboximides) can be considered as “colorful compounds, with a big potential”.

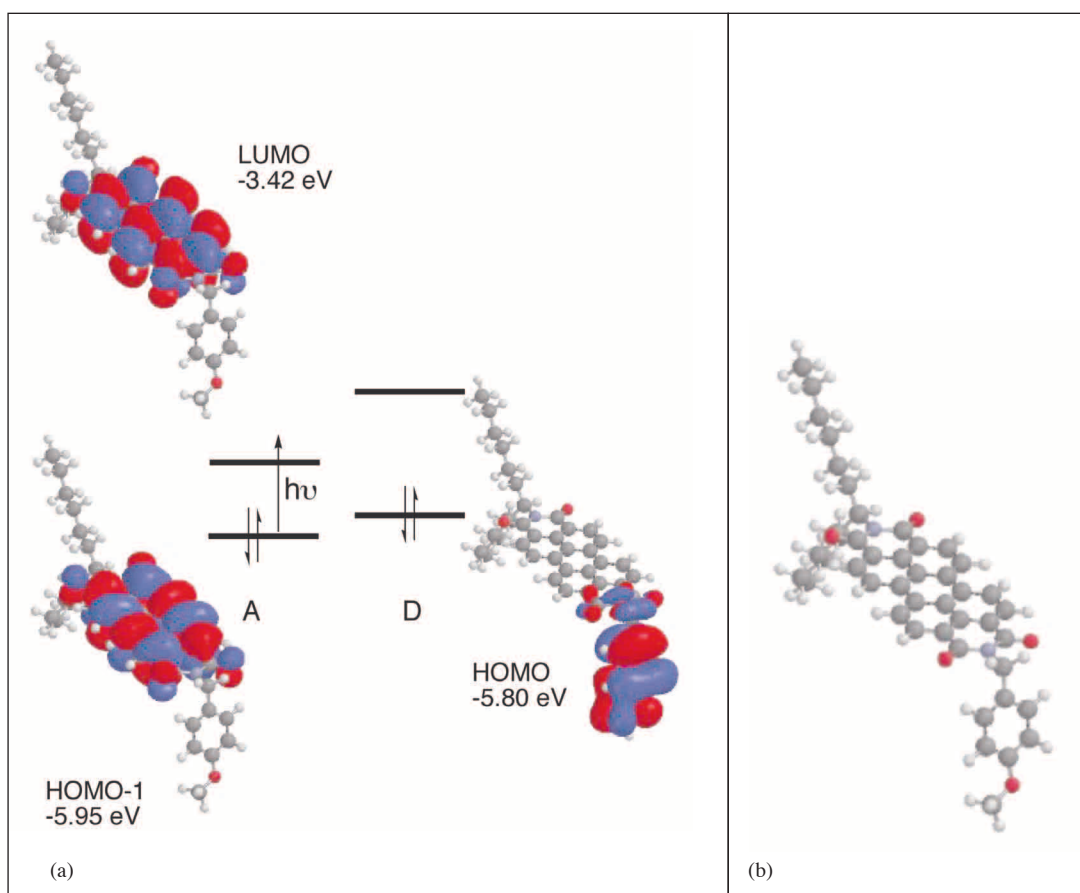


Figure 6. (A) Visualization of the relevant orbitals of **1** as obtained from DFT calculations, (using a value of 0.01 electrons/au³), together with the energies and part of the schematics from Figure 5. (B) 3D structure of compound **1** as obtained from DFT calculations.

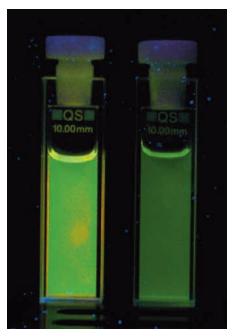


Figure 7. Photograph of 2 solutions of **1** with the same concentration under a UV light (366 nm). The left cuvette displays the un-quenched system in non-polar (cyclohexane) environment. The right cuvette shows the electron transfer quenching in polar (ethylacetate) medium.

Figure 7 visualizes the charge transfer properties of **1**, displaying the dramatic change in luminescence intensity in different environment of the fluorescence-intensity molecular probe **1**.

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