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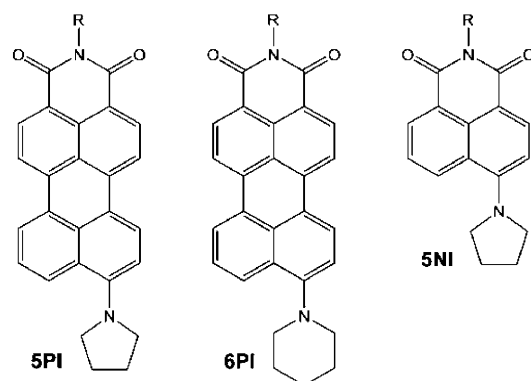
Peter D. Zoon and Albert M. Brouwer*[a]

In N-(2,5-di-tert-butylphenyl)-9-pyrrolidinoperylene-3,4-dicarboximide (**5PI**) the absorption and emission spectra display large solvatochromic shifts, but, remarkably, the Stokes shift is practically independent of solvent polarity. This unique behavior is caused by the extraordinarily large ground-state dipole moment of **5PI**, which further increases upon increasing the solvent polarity, whereas the excited-state dipole moment is less solvent dependent.

In the corresponding piperidine compound, **6PI**, this effect is much less important owing to the weaker coupling between the amino group and the aromatic imide moiety, and in the corresponding naphthalimide, **5NI**, it is absent. The latter shows the conventional solvatochromic behavior of a push–pull substituted conjugated system, that is, minor shifts in absorption and a larger change in the emission energy with solvent polarity.

1. Introduction

Fluorescent dyes that are sensitive to their environment are playing an increasingly important role in ultrasensitive imaging in biology and materials science.^[1,2] Our purpose in this work was to design and characterize dyes that 1) respond to medium polarity by solvatochromic shifts of their fluorescence emission band, and 2) meet all the stringent requirements for single-molecule spectroscopy.^[3,4] We have found that the amino-substituted perylene imides **5PI** and **6PI** (Scheme 1) indeed combine excellent detectability at the single-molecule level with substantial solvatochromic sensitivity.



Scheme 1. Structures of **5PI**, **6PI**, and **5NI**. In experiments: R = 2,5-di-tert-butylphenyl; for computational models: R = H.

On closer inspection, we noted that **5PI** shows a very unusual solvatochromic behavior: Much as in other push–pull substituted conjugated systems, both absorption and emission bands showed a red-shift upon increasing solvent polarity. The Stokes shift, however, was almost solvent independent. It is commonly (and justifiably!) assumed that solvatochromic shifts of electron donor–acceptor systems are primarily due to the solvent responding to the molecular electrostatic potential,

which is different in the ground and excited states, the latter being more polar than the former. The solvatochromic behavior of **6PI** and **5NI**,^[5] which we included in this study for comparison, can be described with this conventional approach; but this fails for **5PI**. We will argue below that in **5PI** the solvatochromic shifts are largely caused by solvent-induced changes in the molecular electronic structure, which lead to a decrease in the S_0 – S_1 energy gap and a decrease in the dipole moment difference upon increasing solvent polarity. This unique behavior is due to the very large ground-state dipole moment of **5PI**, combined with a very large polarizability.

2. Solvatochromism

Compounds in which a substantial change of the molecular dipole moment occurs upon electronic excitation usually reveal large spectral shifts with solvent polarity in absorption, in emission, or in both. These solvatochromic shifts are often used to derive the changes of the dipole moment upon excitation using dielectric continuum models, formulated in the 1950s by Lippert^[6] and Mataga et al.,^[7] on the basis of the earlier work of Ooshika,^[8] Onsager,^[9] and Kirkwood.^[10] Expressions for the solvent-induced changes in the absorption energy and the emission energy relative to their values in vacuum, and the Stokes shift are given in Equations (1)–(3).^[11]

$$E_{\text{abs}} = E_{\text{abs}}^0 - \frac{1}{\rho^3} \left[\vec{\mu}_g (\vec{\mu}_e - \vec{\mu}_g) (f(\epsilon) - f(n^2)) + \frac{1}{2} (\mu_e^2 - \mu_g^2) f(n^2) \right] \quad (1)$$

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[**] Solvatochromism with Solvent-Independent Stokes Shifts.

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$$E_{\text{em}} = E_{\text{em}}^0 - \frac{1}{\rho^3} \left[\vec{\mu}_{\text{e}} (\vec{\mu}_{\text{e}} - \vec{\mu}_{\text{g}}) (f(\varepsilon) - f(n^2)) + \frac{1}{2} (\mu_{\text{e}}^2 - \mu_{\text{g}}^2) f(n^2) \right] \quad (2)$$

$$E_{\text{abs}} - E_{\text{em}} = E_{\text{abs}}^0 - E_{\text{em}}^0 + \frac{1}{\rho^3} \left[(\vec{\mu}_{\text{e}} - \vec{\mu}_{\text{g}})^2 (f(\varepsilon) - f(n^2)) \right] \quad (3)$$

where $\vec{\mu}_{\text{g}}$ and $\vec{\mu}_{\text{e}}$ are the dipole moments in the ground and excited states, respectively; ρ is the cavity radius. The solvent polarity functions of the static dielectric constant ε and the refractive index n are respectively given by Equation (3) and Equation (4)

$$f(\varepsilon) = 2(\varepsilon - 1)/(2\varepsilon + 1) \quad (4)$$

$$f(n^2) = 2(n^2 - 1)/(2n^2 + 1) \quad (5)$$

In the estimation of dipole moment changes from solvatochromic shifts, it is commonly assumed that the dipole moment of the molecule in each of the electronic states is not dependent on solvent polarity. In principle, this is not correct because the electronic polarizability of the molecules means that their dipole moments should be expected to increase with increasing solvent polarity. In practice, other approximations inherent in dielectric continuum models are so severe that the presumably small error due to the neglect of molecular polarizability is usually ignored.^[11] In particular, taking only the continuum dielectric properties, the dielectric constant and the refractive index, as a measure of the solvation energy is not completely satisfactory, as shown by the typically large scatter of the points in plots of excitation energies versus solvent polarity functions. In such plots, groups of solvents with similar chemical natures often tend to cluster. Another serious problem is that the size and shape of the cavity defining the interface between the molecule and the dielectric medium cannot be uniquely defined. Equations (1)–(3) are based on a

model that assumes a spherical cavity. A consistent empirical approach for obtaining the cavity radius ρ is to assume a reasonable density of the molecular material and derive the molecular volume from that. For most molecules, the description as a point dipole in a spherical cavity does not seem to be a very obvious approximation. More complex models of the molecular electric field and cavity shapes have been considered, but from an empirical point of view these are not very helpful because the additional parameters involved cannot be uniquely determined either. For use in quantum chemical calculations, self-consistent reaction-field models have been developed which use semiempirical schemes for defining the molecular surface.^[12,13] In the analysis of experimental data, the simple model underlying Equations (1)–(3) continues to be used in spite of its limitations, 50 years after its introduction.

In the next section, we will first describe our experimental observations. Subsequently, results of quantum chemical calculations including solvent effects using the PCM (polarizable continuum) model will be presented.

3. Solvent Dependence of Absorption and Fluorescence Properties

Absorption and fluorescence spectra of **5NI**, **5PI**, and **6PI**, as well as fluorescence decay times and quantum yields were measured in a series of solvents. These results are presented in Table 1, and are illustrated in Figure 1.

The Stokes shifts of **5NI**, **5PI**, and **6PI** as a function of solvent polarity are plotted in Figure 2.

Analysis of the Stokes shifts according to Equation (3), with a cavity radius of 5.2 Å yields a dipole moment increase $\vec{\mu}_{\text{e}} - \vec{\mu}_{\text{g}}$ of 7.5 D for **6PI**, and ≈ 6.7 D for **5NI** ($r \approx 4.9$ Å). For **5PI**, the Stokes shift is essentially independent of the solvent polarity. According to Equation (3), this would imply that

Table 1. Photophysical properties of **5PI**, **6PI**, and **5NI** in a range of solvents.

| Solvent | Δf^{a} | Abs ^[b] | Fluo ^[b] | 5PI Decay time [ns] | $\Phi_{\text{f}}^{\text{c}}$ | Abs ^[b] | Fluo ^[b] | 6PI Decay time [ns] | $\Phi_{\text{f}}^{\text{c}}$ | Abs ^[b] | Fluo ^[b] | 5NI Decay time [ns] ^[d] | $\Phi_{\text{f}}^{\text{d}}$ |
|-------------------|-----------------------|--------------------|---------------------|----------------------------------|------------------------------|--------------------|---------------------|----------------------------------|------------------------------|---------------------|---------------------|---|------------------------------|
| <i>n</i> -hexane | 0.000 | | | | | | | | | 24.0 ^[c] | 20.8 ^[c] | 6.7 | 0.80 |
| cyclohexane | 0.000 | 18.1 | 15.5; 14.3 | 3.0 | 0.39 | 19.2 | 15.7 | 3.9 | 0.48 | 23.8 | 21.5; 20.4 | | |
| methylcyclohexane | 0.011 | 18.1 | 15.5; 14.3 | 2.8 | 0.37 | 19.2 | 15.7 | 3.9 | 0.48 | 23.8 | 21.5; 20.4 | | |
| cyclooctane | 0.000 | 17.9 | 15.4; 14.2 | 2.8 | 0.41 | 19.2 | 15.6 | 3.5 | 0.42 | 23.8 | 21.5; 20.3 | | |
| toluene | 0.026 | 17.0 | 14.5; 13.4 | 2.9 | 0.46 | 18.6 | 14.9 | 3.3 | 0.40 | | | | |
| diisopropyl ether | 0.290 | 17.4 | 14.7 | 2.9 | 0.33 | 19.0 | 14.9 | 3.4 | 0.40 | | | | |
| diethyl ether | 0.325 | 17.2 | 14.6 | 3.0 | 0.40 | 19.0 | 14.6 | 3.5 | 0.30 | 23.2 | 19.9 | | |
| chloroform | 0.291 | 16.3 | 14.0 | 2.9 | 0.48 | 18.2 | 14.2 | 3.3 | 0.43 | 22.3 | 19.7 | | |
| ethyl acetate | 0.399 | 16.8 | 14.0 | 2.9 | 0.30 | 18.7 | 14.2 | 3.3 | 0.33 | 22.8 | 19.5 | | |
| 2-methyl-THF | 0.405 | 16.8 | 14.1 | 2.9 | 0.37 | 18.7 | 14.3 | 3.1 | | | | | |
| tetrahydrofuran | 0.419 | 16.7 | 13.8 | 2.7 | 0.49 | 18.6 | 14.1 | 3.1 | 0.30 | 22.6 | 19.5 | 7.4 | 0.66 |
| dichloromethane | 0.434 | 16.0 | 13.8 | 3.2 | 0.53 | 18.1 | 13.9 | 3.4 | 0.37 | 22.4 | 19.5 | | |
| acetone | 0.569 | 16.2 | 13.7 | | 0.55 | 18.7 | 13.8 | 3.5 | 0.29 | 22.4 | 19.0 | | |
| ethanol | 0.577 | 15.6 | 13.5 | 2.6 | 0.34 | 18.1 | 13.5 | 2.6 | 0.25 | 22.0 | 18.6 | 0.2; 8.6 | 0.04 |
| methanol | 0.617 | 15.5 | 13.5 | 2.6 | 0.34 | 18.0 | 13.4 | 2.4 | 0.22 | 21.9 | 18.4 | | 0.03 |
| acetonitrile | 0.611 | 15.9 | 13.5 | 3.5 | 0.57 | 18.3 | 13.6 | 3.6 | 0.32 | 22.3 | 18.8 | 1.2; 9.0 | 0.12 |

[a] $\Delta f = f(\varepsilon) - f(n^2)$, see Equations (4) and (5). [b] Absorption and fluorescence maxima in 10^3 cm^{-1} . [c] Using Perylene Red as the standard ($\Phi_{\text{f}} = 0.96$),^[33] [d] from Saha et al., ref. [5].

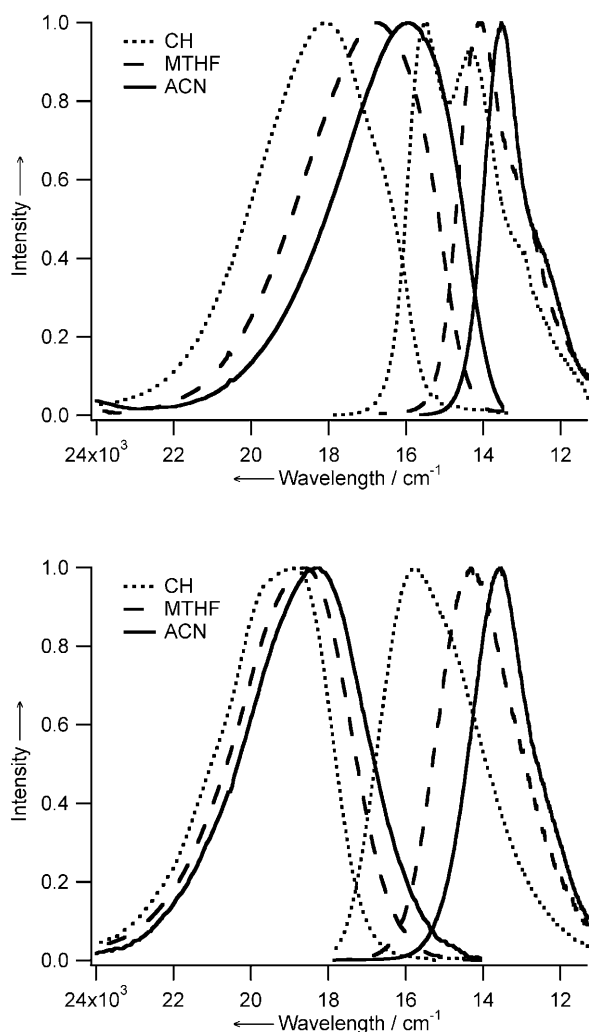


Figure 1. Absorption and emission spectra of A) **5PI** and B) **6PI** in cyclohexane (CH), methyltetrahydrofuran (MTHF), and acetonitrile (ACN) as representative solvents of low, medium, and high polarity, respectively.

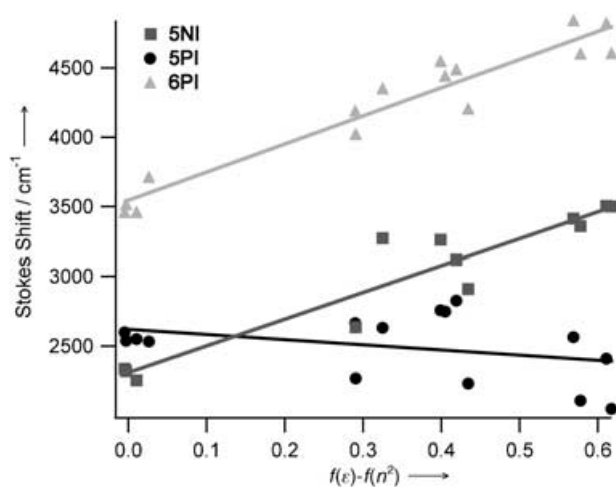


Figure 2. Plot of the Stokes shifts of **5NI**, **5PI**, and **6PI** as a function of $f(\epsilon) - f(n^2)$.

$\mu_e = \mu_g$, but this cannot be reconciled with the large solvatochromic shifts observed.

The observation of large solvatochromic shifts in absorption and emission of **5NI**, **5PI**, and **6PI** indicates that the excited-state dipole moments of these molecules are larger than those of the ground states. Hence, the term "charge-transfer transition" should apply to the observed transitions. Typically, such transitions are associated with large solvent reorganization energies, which result in an increase in the nonradiative decay rates,^[5,14–16] and an increase in the width of the emission bands,^[17] with increasing solvent polarity. Remarkably enough, the data in Table 1 reveal no clear correlation of the decay times of **5PI** and **6PI** with solvent polarity or energy gap, and the band widths (Figure 3) in fact show a trend *opposite* to that expected. For **5NI**, the width of the emission band varies between 2800 and 3200 cm⁻¹, with no apparent correlation with the emission energy.

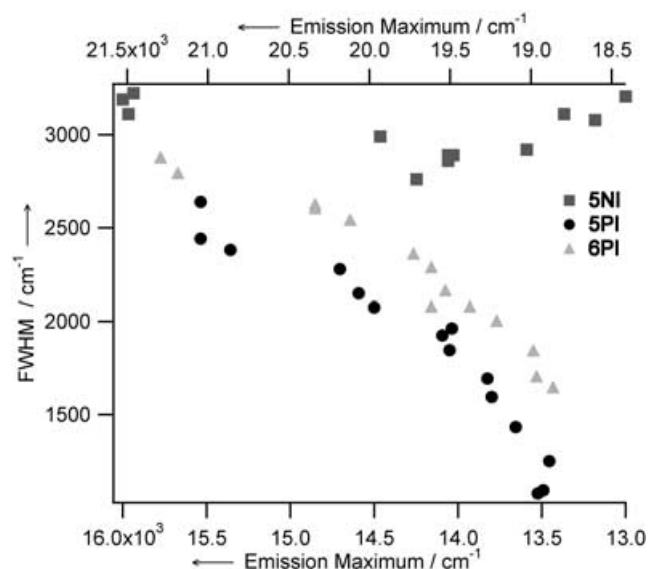


Figure 3. Band width (full width at half maximum, FWHM) as a function of emission energy of **5NI** (top axis), **5PI**, and **6PI** (bottom axis).

In order to understand these very unusual observations, in the next section we discuss the electronic structures of the compounds, starting from a basic level, and subsequently considering the results of *ab initio* calculations.

4. Electronic Structure

The dipole moments of the electronic states of the amino-substituted imides are governed largely by electron donor–acceptor or mixing. Let us regard the amino group as the electron donor, and the aromatic imide unit as the acceptor. With the interaction turned off, the localized amino lone pair will constitute the highest occupied molecular orbital (HOMO), the localized imide the acceptor. HOMO–LUMO (lowest unoccupied molecular orbital) excitation will lead to the transfer of an electron from donor to acceptor, producing a charge-separated excited state with a large dipole moment. Taking a distance of

about 7 Å between the amino nitrogen and the center of the aromatic ring as the donor–acceptor distance, a complete charge separation will lead to a dipole moment of about 30 D. The ground state in this hypothetical situation will have a small dipole moment, caused by the differences in electronegativity of the atoms, pointing towards the imide group.

Orbital interaction and mixing between the hypothetical localized orbitals of the amino group and the aromatic imide group will lead to a transfer of electron density from the amino group to the imide in the HOMO. This will make the ground state (two electrons in the HOMO) dipolar, with a partial positive charge on the amino group and a partial negative charge on the imide unit. The HOMO–LUMO excited state, at the same time, will have a smaller dipole moment compared to the hypothetical case of no orbital mixing, but the excited-state dipole moment will still be larger than that of the ground state. Typical examples of HOMO and LUMO orbitals were calculated for model systems of **5PI** and **6PI** in which the *N*-aryl groups were replaced by hydrogen atoms. A difference between the naphthalene and perylene aromatic linkers is that the latter have occupied orbitals of higher energy, and unoccupied orbitals of lower energy, which favors the interaction between donor and acceptor. Moreover, the effective donor–acceptor distance is larger in perylene imides than in naphthalene imides. As a result, the ground-state dipole moments (computed with *ab initio* methods, see below) are systematically larger for the perylene imides than for the naphthalimides.

For an optimal orbital interaction, the overlap of the amino “lone pair” with the π -system should be maximized. This is achieved when the amino group adopts an sp^2 hybridization, and a coplanar structure of the aromatic ring, the nitrogen atom, and the other two substituents attached to it. In the ground state, an energetic price has to be paid for the distortion of the amino group from its “natural” pyramidal configuration, which limits the extent of orbital interaction. In this respect, differences emerge between the pyrrolidine and piperidine electron donor groups, the former being less pyramidal, and less prone to be twisted out of the plane of the aromatic ring.

The molecular geometries and the electronic structures of **5PI**, **6PI**, and **5NI** were calculated using a (by now conventional) hybrid Hartree–Fock/density functional method (B3LYP/6-31G*).^[18] In these calculations, the aromatic substituents on the imide nitrogen were replaced by a hydrogen atom. It is well-known that the nitrogen substituent has very little effect on the photophysical behavior of this class of compound. The HOMO and LUMO both have a node on the nitrogen atom of the imide (see Figure 4). Solvent effects were taken into account using the PCM.^[13] Excitation energies were calculated using time-dependent density functional theory (TDDFT).^[19] PCM calculations were carried out with the ground-state equilibrium polarization, which corresponds to vertical excitation. In addition, TDDFT calculations were performed with the reaction field corresponding to the excited electronic state.^[19] This gives only an indication of the excited-state relaxation, because the geometry is not optimized. To obtain insight into

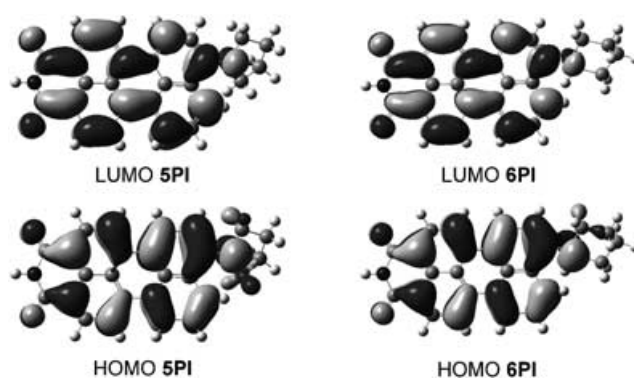


Figure 4. HOMO and LUMO of model systems for **5PI** and **6PI** (B3LYP/6-31G*, no solvent). In the HOMOs, there is a larger contribution of the amino group than in the LUMOs; for the imide C=O groups, the opposite is true.

the latter, configuration interaction calculations were performed with single excitations (CIS/6-31G*).^[20] The CIS optimized geometry was then used to calculate the vertical transition energy corresponding to emission from the relaxed excited-state using TDDFT. Results of the calculations for the lowest-energy conformation of each compound are presented in Table 2 and Figure 5.

Geometrical parameters of **5PI**, **6PI**, and **5NI** are graphically presented in Figure 5, and reported in more detail in the Supporting Information. In agreement with expectation, the amino groups in all three compounds adopt an intermediate hybridization between sp^2 ($\Sigma N = 360^\circ$) and sp^3 ($\Sigma N \approx 330^\circ$). In the piperidine compound **6PI**, the amino group is more pyramidal than in **5PI** and **5NI**. The plane of the amino group is somewhat twisted with respect to the plane of the aromatic rings, especially for **6PI**. Another important geometric indicator of the interaction between the amino group and the aromatic imide unit is the C–N bond length. This is substantially smaller for the pyrrolidine compounds **5NI** and **5PI** than for the piperidine compound **6PI**. In all three molecules, increasing the solvent polarity enhanced the donor–acceptor interaction, as seen from the decrease in pyramidalization, the decrease in the C=C–C–N dihedral angles, and the decrease in the C–N bond length.

The main change in geometry upon excitation is in the C–N bond length: It becomes shorter in all three molecules. According to the CIS calculations, the amino groups retain a similar degree of pyramidalization as in the ground state and the dihedral angles increase somewhat. It should be kept in mind that the results for the ground and excited states cannot be directly compared, because different computational models were used for the two states and these are likely to have different systematic errors.

Table 2 lists the dipole moments calculated for the different molecules in the ground state, using B3LYP/6-31G*, and in the lowest excited state, using CIS/6-31G*. Some common trends catch the eye:

- The dipole moments increase on going from the gas phase to increasingly polar solvents. For **5PI**, this increase (57%) is larger than for **6PI** (46%) and **5NI** (42%).

Table 2. Results of quantum chemical calculations on **5PI**, **6PI**, and **5NI**. Dipole moments of the ground state μ_g (B3LYP/6-31G*) and excited state μ_e (CIS/6-31G*) in Debye. Excitation energies in electron volts.

| Compound ^[a] | Ground-state geometry | | | | Excited-state geometry | | |
|-------------------------|-----------------------|------------------------|--------------------------|------------------------|------------------------|--------------------------|------------------------|
| | solvent | μ_g ^[b] | E_{exc} ^[c] | μ_e ^[d] | μ_e ^[e] | E_{exc} ^[f] | μ_g ^[g] |
| 5PI | none | 11.5 | 2.347 | 13.6 | 13.6 | 2.209 | 11.7 |
| | cyclohexane | 13.3 (13.8) | 2.198 (2.198) | 16.4 | 15.5 | 2.065 | 14.5 |
| | THF | 16.7 (15.3) | 2.149 (2.252) | 19.0 | 18.7 | 2.157 | 17.5 |
| | acetonitrile | 18.0 (16.1) | 2.140 (2.234) | 19.9 | 19.8 | 2.152 | 18.7 |
| 6PI | none | 9.2 | 2.431 | 11.3 | 10.8 | 2.286 | 9.3 |
| | cyclohexane | 10.8 (10.6) | 2.292 | 13.4 | 12.8 | 2.138 | 11.1 |
| | THF | 12.7 (11.9) | 2.241 (2.129) | 15.2 | 14.8 | 1.994 | 13.2 |
| | acetonitrile | 13.4 (12.5) | 2.231 (2.063) | 16.5 | 15.6 | 1.936 | 14.0 |
| 5NI | none | 8.5 | 3.160 | 10.6 | 10.4 | 2.895 | 8.7 |
| | cyclohexane | 9.8 (9.6) | 3.041 | 12.3 | 12.0 | 2.801 | 10.2 |
| | THF | 11.5 (10.8) | 2.982 (2.907) | 13.8 | 13.8 | 2.691 | 11.8 |
| | acetonitrile | 12.1 (11.2) | 2.966 (2.878) | 14.8 | 14.0 | 2.644 | 12.3 |

[a] *N*-aryl groups replaced by H atoms. [b] Corresponding to optimized geometry; numbers in parentheses are the dipole moments in solution for the gas-phase geometry. [c] TDDFT, non-equilibrium polarization, that is, corresponding to vertical excitation; numbers in parentheses correspond to equilibrium polarization. [d] CIS dipole moment at the ground-state geometry (non-equilibrium solvation). [e] CIS dipole moment at the excited-state geometry. [f] TDDFT, corresponding to the optimized excited-state geometry; polarization in equilibrium with the excited-state electron density. [g] Ground-state dipole moment (B3LYP/6-31G*) at the CIS/6-31G* geometry.

- Optimization of the ground-state geometries in solvents leads to an increase in the dipole moment. Also, this effect is strongest for **5PI**, for example in acetonitrile the increase is 12% whereas it is only 7% for **6PI** and 8% for **5NI**.
- The ground-state dipole moments at the CIS optimized geometries are slightly larger than those at the ground-state optimized geometries.
- The excited-state (CIS) dipole moments are larger than the ground-state dipole moments for the same species. This is in agreement with the anticipated charge-transfer nature of the electronic transition, but the numbers cannot be reliably compared because of the different computational methods used for the ground and excited states.
- The excited-state dipole moments do not change significantly upon optimization of the excited-state geometry.

In most cases, the excitation energy decreases when allowing relaxation of the polarization in tetrahydrofuran (THF) and acetonitrile, and when the excited-state geometry is optimized. This would be expected in the case of a charge-transfer transition, in which the dipole moment, and hence the electrostatic interaction with the medium, increases upon excitation. An exception, however, is the case of **5PI**. In THF and in acetonitrile, using the reaction field of the excited state for the calculation of the vertical excitation energy gives an *increase* in the excitation energy. *This suggests that the excited state is less polar than the ground state.* Unfortunately, gradients for the TDDFT model^[21] in combination with solvation models have not yet been implemented in programs which are available to us, so that neither calculations of the relaxed densities nor optimizations of the geometries were possible. Optimization of excited **5PI** with CIS led to a smaller energy difference with the ground state in the gas phase and cyclohexane, but not in THF or acetonitrile.

5. Discussion and Conclusions

Most solvatochromic molecules known to date show either a large shift in their absorption or in their emission spectra. When $\mu_g \gg \mu_e$ or $\mu_e \gg \mu_g$, Equation (1) and Equation (2) can be approximated well by simple functions which permit the dipole moment of the dipolar state to be derived from a plot of the absorption or emission energy versus $f(\epsilon) - f(n^2)/2$.

When the ground-state dipole moment is very large and the excited-state dipole moment much smaller, as in the famous betaine dye ET(30),^[22–24] a shift to higher absorption energies with increasing solvent polarity is observed (negative solvatochrom-

ism). A large solvent dependence of the Stokes shift would still be expected in such a case; but, unfortunately, ET(30) and similar compounds are virtually non-fluorescent.^[25] On the other hand, when $\mu_e \gg \mu_g$, there is a large solvatochromic shift in emission,^[26,27] but almost no solvatochromic shift in absorption because only the instantaneous electronic polarization of the solvent can respond to the change in the molecular electrostatic potential upon excitation, and this property is almost the same for all organic solvents ($n^2 \approx 2$).^[28] Push–pull conjugated compounds form an intermediate class.^[29–31] Their ground-state dipole moments are large enough to induce a solvent polarization which interacts more strongly with the molecules in the excited state because the dipole moments are in the same direction and the excited-state dipole moment is larger, which explains why there is a modest solvatochromic shift in absorption. The fluorescence solvatochromic shift is larger than the shift in absorption because it is driven by the larger excited-state dipole moment. **5NI** and **6PI** can be seen as representatives of this class.

Owing to a combination of efficient donor–acceptor interaction and large donor–acceptor distance, **5PI** has a much larger ground-state dipole moment than **5NI** or **6PI**. All three compounds show an increase in ground-state dipole moment upon increasing solvent polarity, but this effect is much bigger for **5PI** than for **5NI** or **6PI**. As a result, the dipole moment increase upon excitation vanishes in **5PI**, especially in more polar solvents. Simultaneously, the structural relaxation, both intramolecular and in solvation coordinates, decreases, which results in a narrowing of the emission bands. Nevertheless, there is still a solvatochromic shift in **5PI**, but this is to a large extent due to the solvent-enhanced donor–acceptor mixing, which reduces the HOMO–LUMO gap!

We are presently not aware of any other molecule for which this effect has been described. Miller et al.^[32] reported on simi-

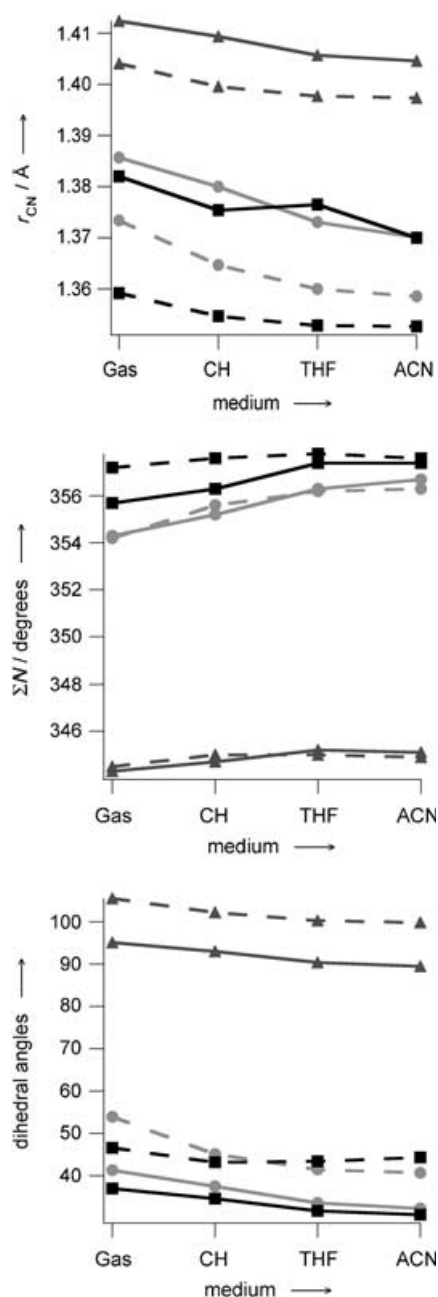


Figure 5. Computed geometrical parameters of 5NI (■), 5PI (●), and 6PI (▲) in the ground state (B3LYP/6-31G*, —) and lowest excited state (CIS/6-31G*, ---) in different media: isolated molecule, cyclohexane, THF, and acetonitrile; r_{CN} is the length of the bond between the nitrogen of the amino group and the aromatic ring; ΣN is the sum of the bond angles of the amino nitrogen; and "dihedral angle" is the sum of the C=C–N–C dihedral angles as a measure of the co-planarity of the aromatic ring and the amino group.

lar perylene imide derivatives, with additional substituents in the 1 and 6 positions. They did not describe the solvatochromic behavior of the absorption spectra, but the spectra of their piperidine and pyrrolidine compounds in toluene resemble those of 6PI and 5PI, respectively, with a small red-shift due to the bay substitution. In principle, the observation of near-identical solvatochromism in absorption and emission

should be possible in other compounds with the same molecular and electronic structural features: strong coupling between donor and acceptor; a large ground-state dipole moment; and a large polarizability. In 5PI, the large polarizability is in part due to the possibility of structural change around the amino group. In contrast to 5PI, 5NI behaves as a conventional push–pull system, with a modest solvatochromic shift in absorption and a larger solvatochromic shift in emission. The solvatochromic behavior of 6PI is similar to that of 5NI, but the solvent dependence of its band shape resembles that of 5PI. The narrowing of the emission band upon increasing solvent polarity is tentatively attributed to a smaller geometry difference between the relaxed S_1 and S_0 states.

Further studies of the photophysical properties of these compounds, and their application as solvatochromic probes and in single-molecule studies^[34] are in progress.

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Keywords: density functional calculations • donor–acceptor systems • electronic structure • solvatochromism • UV/Vis spectroscopy

- [1] K. A. Willets, O. Ostroverkhova, M. He, R. J. Twieg, W. E. Moerner, *J. Am. Chem. Soc.* **2003**, 125, 1174.
- [2] D. A. Higgins, M. M. Collinson, G. Saroja, A. M. Bardo, *Chem. Mater.* **2002**, 14, 3734.
- [3] W. E. Moerner, D. P. Fromm, *Rev. Sci. Instrum.* **2003**, 74, 3597.
- [4] M. Bohmer, J. Enderlein, *ChemPhysChem* **2003**, 4, 793.
- [5] S. Saha, A. Samanta, *J. Phys. Chem. A* **2002**, 106, 4763.
- [6] E. Lippert, *Z. Naturforsch., A: Phys. Sci.* **1955**, 10, 541.
- [7] N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **1956**, 29, 465.
- [8] Y. Ooshika, *J. Phys. Soc. Jpn.* **1954**, 9, 594.
- [9] L. Onsager, *J. Am. Chem. Soc.* **1936**, 58, 1486.
- [10] J. G. Kirkwood, *J. Chem. Phys.* **1939**, 7, 911.
- [11] P. Suppan, *J. Photochem. Photobiol., A* **1990**, 50, 293.
- [12] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, 55, 117.
- [13] M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, 117, 43.
- [14] S. I. Van Dijk, P. G. Wiering, C. P. Groen, A. M. Brouwer, J. W. Verhoeven, W. Schuddeboom, J. M. Warman, *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2107.
- [15] R. J. Willemse, J. J. Piet, J. M. Warman, F. Hartl, J. W. Verhoeven, A. M. Brouwer, *J. Am. Chem. Soc.* **2000**, 122, 3721.
- [16] R. J. Willemse, D. Theodori, J. W. Verhoeven, A. M. Brouwer, *Photochem. Photobiol. Sci.* **2003**, 2, 1134.
- [17] R. A. Marcus, *J. Phys. Chem.* **1989**, 93, 3078.
- [18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma,

- G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cio-slawski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, USA, **2003**.
- [19] M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, *115*, 4708.
- [20] R. Cammi, B. Mennucci, J. Tomasi, *J. Phys. Chem. A* **2000**, *104*, 5631.
- [21] F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2002**, *117*, 7433.
- [22] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319.
- [23] C. Reichardt, *Pure Appl. Chem.* **2004**, *76*, 1903.
- [24] T. Ishida, P. J. Rossky, *J. Phys. Chem. A* **2001**, *105*, 558.
- [25] S. A. Kovalenko, N. Eilers-Konig, T. A. Senyushkina, N. P. Ernstring, *J. Phys. Chem. A* **2001**, *105*, 4834.
- [26] R. M. Hermant, N. A. C. Bakker, T. Scherer, B. Krijnen, J. W. Verhoeven, *J. Am. Chem. Soc.* **1990**, *112*, 1214.
- [27] T. Scherer, W. Hielkema, B. Krijnen, R. M. Hermant, C. Eijkelhoff, F. Kerkhof, A. K. F. Ng, R. Verleg, E. B. v. d. Tol, A. M. Brouwer, J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 535.
- [28] B. Krijnen, H. B. Beverloo, J. W. Verhoeven, C. A. Reiss, K. Goubitz, D. Heijdenrijk, *J. Am. Chem. Soc.* **1989**, *111*, 4433.
- [29] A. K. Singh, G. R. Mahalaxmi, *Photochem. Photobiol.* **2000**, *71*, 387.
- [30] Y. V. Il'ichev, K. A. Zachariasse, *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 625.
- [31] C. Peinado, E. F. Salvador, F. Catalina, A. E. Lozano, *Polymer* **2001**, *42*, 2815.
- [32] S. E. Miller, Y. Y. Zhao, R. Schaller, V. Mulloni, E. M. Just, R. C. Johnson, M. R. Wasielewski, *Chem. Phys.* **2002**, *275*, 167.
- [33] G. Seybold, G. Wagenblast, *Dyes Pigm.* **1989**, *11*, 303.
- [34] P. D. Zoon, A. M. Brouwer, R. A. L. Vallee, J. Hofkens, F. C. De Schryver, unpublished results.

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