



Theoretical and experimental study on the intramolecular charge transfer excited state of the new highly fluorescent terpyridine compound

Peng Song^{a,c}, Shi-Guo Sun^b, Jian-Yong Liu^a, Yong-Qian Xu^b, Ke-Li Han^{a,*}, Xiao-Jun Peng^{b,**}

^a State Key Lab of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

^c Graduate School of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 26 March 2009

Received in revised form 8 July 2009

Accepted 7 August 2009

Keywords:

Excited state

Twisted intramolecular charge transfer

Relaxation dynamics

Fluorescence spectra

ABSTRACT

Experimental and theoretical methods have been used to investigate the relaxation dynamics and photophysical properties of the donor–acceptor compound 4'-(4-N,N-diphenylaminophenyl)-2,2':6',2''-terpyridine (DPAPT), a compound which is found to exhibit efficient intramolecular charge transfer emission in polar solvents with relatively large Stokes shifts and strong solvatochromism. The difference between the ground and excited state dipole moments ($\Delta\mu$) is estimated to be 13.7 D on the basis of Lippert–Mataga models. To gain insight into the relaxation dynamics of DPAPT in the excited state, the potential energy curves for conformational relaxation are calculated. From the frontier molecular orbital (MO) pictures at the geometry of the twisted ICT excited state, the intramolecular charge transfer mainly takes place from HOMO (triphenylamine) to LUMO (terpyridine) in this donor–acceptor system.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Numerous theoretical and experimental studies have been used to explore the origin of the intramolecular charge transfer (ICT) fluorescence [1–12], since the first observation of the dual fluorescence phenomenon of 4-(N,N-dimethylamino)benzonitrile (DMABN) in polar solvents by Lippert et al. [1], whose work plays a key role in the photophysics of donor–acceptor π -conjugated (D - π - A) compounds. In view of the importance of the photoinduced ICT processes, the interest in molecular donor–acceptor [4–6,13] and different position substituted [14] systems has increased significantly, they have been widely used in molecular switches [15,16], dye-sensitized solar cells (DSSCs) [17], fluorescence sensors and as components for supramolecular assemblies [18–20].

The 2,2':6',2''-terpyridine (tpy) is well-known for its good coordination ability due to the suitable arrangement of ring nitrogens. However, the fluorescence properties of tpy ligands themselves have been less studied for use as fluorescent sensors, possibly due to the expected lack of selectivity and perhaps also to the fact that few tpy are strongly emissive at wavelengths other than in the UV, with short-wavelength excitation being required. It was found that changes in the molecular structure

and conjugated system can induce very different optical and physical properties in D - π - A compounds. A variety of tpy derivatives have been reported to date [18,21,22]. Exceptional tpy derivatives include 4'-(9-anthryl)-tpy [23] which has moderate quantum yield ($\Phi = 0.5$), 5,5'-bis(4-methoxy-2,6-dimethylphenyl)-tpy [24] with markedly strong ($\Phi = 0.85$) blue fluorescence, and 4'-phenyl-tpy derivatives which have moderate quantum yields ($\Phi = 0.2$ – 0.4) and whose fluorescence is changed by the intramolecular charge transfer process [13]. Several years ago, Goodall and Williams have reported on the use of palladium-catalysed cross-couplings of aryl boronates with 4'-bromoterpyridine, to construct novel, 4'-substituted terpyridines in high yield [25]. In particular, this methodology has been used to prepare the compound 4'-(4-N,N-diphenylaminophenyl)-2,2':6',2''-terpyridine, a highly fluorescent new ligand whose emission is distinctively affected by binding with zinc ions [26]. From the fluorescence spectra, DPAPT was found to exhibit efficient ICT emission in polar solvents with a large Stokes shift and strong solvatochromism. Two main models have been proposed to explain the mechanism of formation of the intramolecular charge transfer state, twisted intramolecular charge transfer (TICT) and planar intramolecular charge transfer (PICT) [3]. To get a better understanding of the formative mechanism, the steady state absorption and fluorescence spectra of DPAPT system are discussed in detail. Also, the potential energy curves as a function of the twisting angle (φ and θ , as shown in Scheme 1) were also studied by the time-dependent density functional theory (TDDFT) method to investigate the conformational relaxation dynamics of DPAPT in the excited state.

* Corresponding author. Tel.: +86 411 84379195 fax: +86 411 84675584.

** Corresponding author.

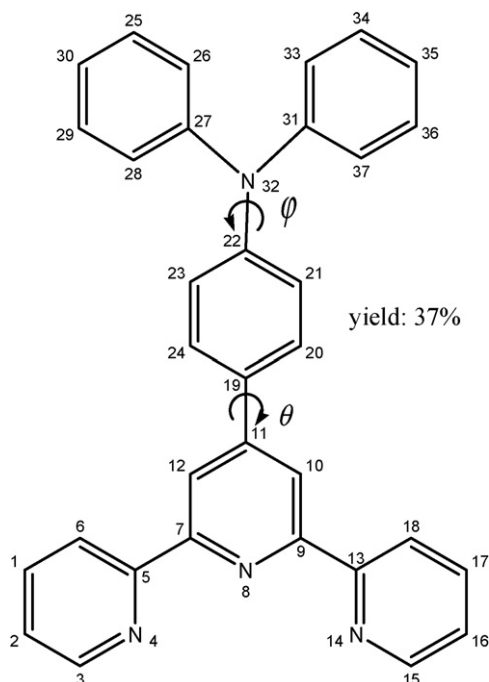
E-mail addresses: klhan@dicp.ac.cn (K.-L. Han), pengxj@dlut.edu.cn (X.-J. Peng).

2. Experimental and computational methods

Synthesis of DPAPT: 2-acetylpyridine, N,N-diphenylaminophenyl aldehyde, and solid NaOH were ground for 15 min in a mortar. The resultant yellow solid powder was transferred into a flask containing ammonium acetate and acetic acid, and refluxed for 2 h. Cooling to room temperature, the pH of the reaction mixture was adjusted to 5 by NaOH. The precipitated solid product was collected by filtration and purified on a alumina column (65% yield). The solid product was dissolved in absolute ethanol, refluxed for 1 h over 10% Pd/C catalyst, and the hydrazine hydrate was then added and the mixture was refluxed for another 1 h. The Pd/C catalyst was removed by hot filtration and washed with CH₂Cl₂. The filtrate and the washings were combined and evaporated in vacuum. The residue was further purified by recrystallization from ethanol. We obtain the desired compound in 37% yield, and the molecular structure was shown in Scheme 1.

The solute DPAPT was dissolved in *n*-hexane, ethanol, dichloromethane, acetonitrile, and methanol at room temperature (ca. 22 °C) with a concentration of 1×10^{-4} M. The absorption spectra of DPAPT in all of the solvents were run on a UV–vis absorption spectrophotometer (HP8453, Hewlett-Packard Corp). The fluorescence spectra were measured with a C-700 spectrofluorometer (Photo Technology International Corp).

All the electronic structure calculations were carried out using the TURBOMOLE program suite [27–31]. The geometry optimizations of the isolated monomers considered here for the ground state were performed using density functional theory (DFT) with Becke's three-parameter hybrid exchange function and a Lee–Yang–Parr gradient-corrected correlation function (B3-LYP function) [28]. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis set throughout [30]. The potential energy curves were calculated using time-dependent density functional theory (TD-DFT) with B3-LYP hybrid functions and the TZVP basis set. Fine quadrature grids 4 were also employed [29,31]. The convergence thresholds for the ground state optimization were reset to be 10^{-8} (default settings are 10^{-6}).



Scheme 1. Chemical structure of the DPAPT compound.

Table 1

Photophysical properties of DPAPT in solvents of varying polarity.

Solvent	λ_{abs} (nm)	λ_{fl} (nm)	$\Delta\nu_{1/2}$ (cm ⁻¹)	$\Delta\nu_{\text{st}}$ (cm ⁻¹)
<i>n</i> -Hexane	354	393	2525	2803
Dichloromethane	360	476	3314	6769
Acetonitrile	357	489	3763	7561
Ethanol	362	505	3882	7822
Methanol	359	524	4257	8771

3. Results and discussion

3.1. Steady-state electronic spectra

The ground state absorption spectra of DPAPT recorded in *n*-hexane, dichloromethane, acetonitrile, and various alcohols, display an intense long-wavelength absorption band around 360 nm. The corresponding absorption maxima (λ_{abs}) are reported in Table 1, and typical spectra are presented in Fig. 1. In addition, the absorption maxima shows a small red shift with increasing solvent polarity, indicating that the ground state and the FC excited state have similar dipole moment. The absorption band can be attributed to electronic transitions from the HOMO to an unoccupied orbit which is the LUMO at the local excited (LE) state structure (vide infra).

The fluorescence maximum and the shape of the fluorescence band are very sensitive to solvent characteristics. The fluorescence spectra are structured in hexane but the structure become unclearly in more polar solvents such as in acetonitrile. In addition, when we pay attention to methanol, we can see that there is a small peak around 425 nm, this can be expected to emit from the LE state, because of methanol can hydrogen bond to the N atom of the diphenylamino [32]. Unlike the absorption spectra, the fluorescence spectra show a strong solvatochromic red shift with increasing solvent polarity, indicating that the asymmetrically charge-distributed state gains intramolecular charge transfer (ICT) character for the fluorescent state. It can be seen from Fig. 2 that the size of the solvatochromic shifts strongly depend on the polarity of the solvent and the shape of the structureless fluorescence spectra in polar solvents are of normal Gaussian shape. The detailed emission maxima (λ_{fl}) as well as the Stokes shifts ($\Delta\nu_{\text{st}}$), and the half bandwidths ($\Delta\nu_{1/2}$) are collected in Table 1.

To determine the excited state dipole moment μ_e of the molecules, the ν_{st} are plotted against the polarity parameter $f(\epsilon, n)$, as shown in Fig. 3, using the Lippert–Mataga Eqs. (1)–(3) [33,34], where ϵ is the dielectric constant, n is the refractive index, ρ is the solvent cavity (Onsager) radius of the solute [35], and the applicable

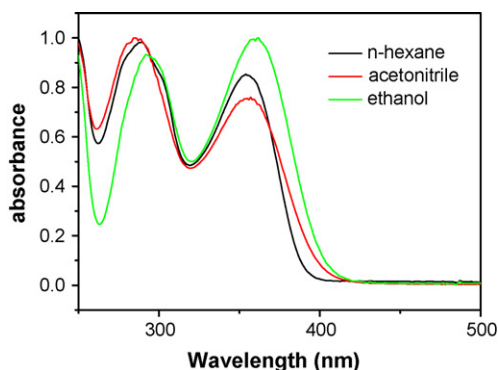


Fig. 1. Ground state absorption spectra of DPAPT in *n*-hexane, acetonitrile, and ethanol.

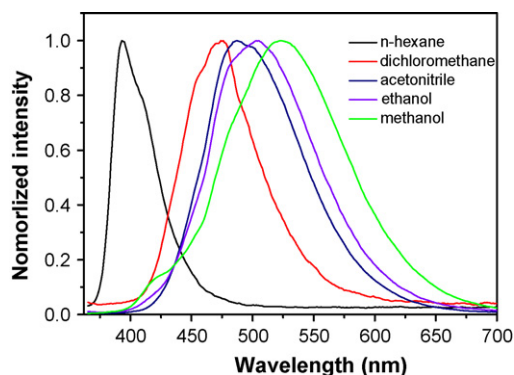


Fig. 2. Fluorescence spectra of DPAPT in *n*-hexane, dichloromethane, acetonitrile, ethanol and methanol.

polarity function $f(\epsilon, n) = f(\epsilon) - f(n^2)$.

$$\Delta v_{st} = \frac{1}{4\pi\epsilon_0} \frac{2}{hc\rho^3} (\mu_e - \mu_g)^2 f(\epsilon, n) + \text{const} \quad (1)$$

$$f(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1} \quad (2)$$

$$f(n^2) = \frac{n^2 - 1}{2n^2 + 1} \quad (3)$$

By applying the partial volume addition method, as suggested by Edward, the Onsager cavity radius, ρ , is estimated to be 4.67 Å [36]. Substituting the value of ρ , the absolute value of $\Delta\mu$ is calculated to be 13.66 D. The theoretical value of μ_g , which was calculated by geometry optimization using the Hartree–Fock method with the TZVP basis set in the TURBOMOLE program suite [37], is 3.99 D whose dipole moment is parallel to the long axis of the molecule with the amplitude of 1.5710 a.u. The Stokes shift v_{st} depending on the solvent polarity, reveals a larger charge transfer character for the triphenylamine derivatives in the lowest excited state [38–40]. Also, the large dipole moment change possibly indicates that, for DPAPT in all solvents, the conformation of the ICT state after excitation attains a more stable state (named the TICT state, which is highly polar) [3]. Because in polar solutions the configuration with the maximum dipole moment is preferentially stabilized, so that for strong dipolar stabilization, the excited state corresponds to twisted structure [41]. We must comment that considering so many molecules, which the ICT state corresponds to the planar structure (PICT model), have larger dipole moment as put forward by Zachariasse et al. [7,10], so the calculation of potential energy curves becomes a key factor in determining the conformation of the ICT state.

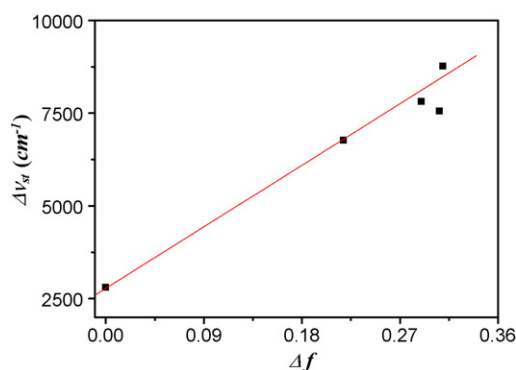


Fig. 3. Solvatochromic plot of Stokes shift v_{st} for DPAPT as a function of solvent polarity parameter Δf .

3.2. Calculated potential energy curves and molecular orbits (MOs)

For the majority of simple organic molecules containing electron donating and accepting moieties, the charge separation is more favorable in a twisted conformation, i.e., if the molecular planes of the two moieties are positioned in perpendicular configurations with respect to each other [3,41]. In DPAPT, the triphenylamine serves as donor and joins together with tpy to form a *D*- π -*A* structure. Once the molecule is excited, the initial excitation may be located on the benzene ring (see Fig. 5a), but after that it begins to delocalize. There are two decay routes for the population in the excited state: one is relaxation to the lower levels of the ICT state and the other is direct relaxation to the ground state accompanied by emission of a photon.

Accordingly, we will firstly discuss in this section the potential energy curve of conformational relaxation via molecular twisting: (i) twisting of only the diphenylamino group (φ); or (ii) twisting of the triphenylamine group with respect to the tpy group (θ). For the construction of the energy curves, the geometry is kept frozen to that optimized for the ground state, and the only variable parameter is the twisting angle, ranging from 0° to 180° in steps of 10°. The results for the ground state and the two lowest excited states of the DPAPT are presented in Fig. 4.

In the ground state, DPAPT prefers to be non-planar structure, due to steric hindrance, with the dihedral angles 38° and 35.4° formed by atoms 23–22–32–27 and 12–11–19–24 (Scheme 1), respectively. Upon photoexcitation, DPAPT can be initially excited to the S_1 (LE) state with conformational geometry similar to the ground state (unrelaxed). The twisting angle φ potential energy curve shows that the energies are almost constant from 30° to 90°, with a small energy gap with the minimum energy at 60° (see Fig. 4a). In contrast, the twisting angle θ potential energy curve

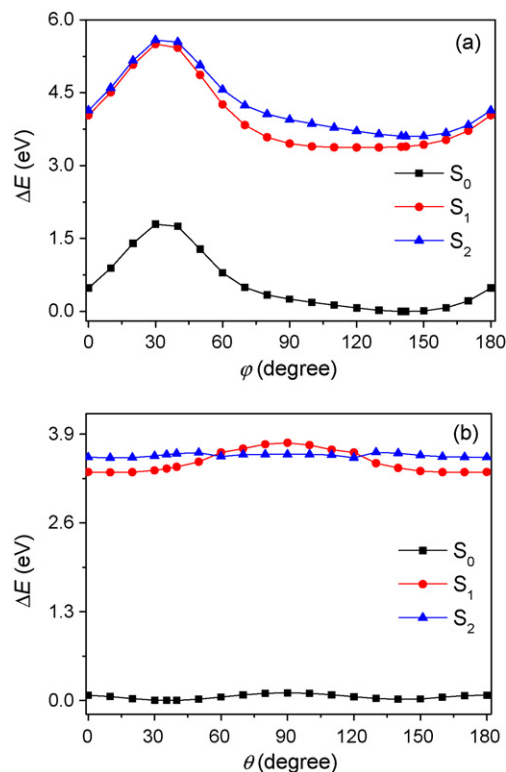


Fig. 4. Ground and the low-lying singlet excited state potential curves (energy relative to the minimum of the ground state) as a function of the twisting angle of the φ -diphenylamino (a) and of the θ -triphenylamine group (b).

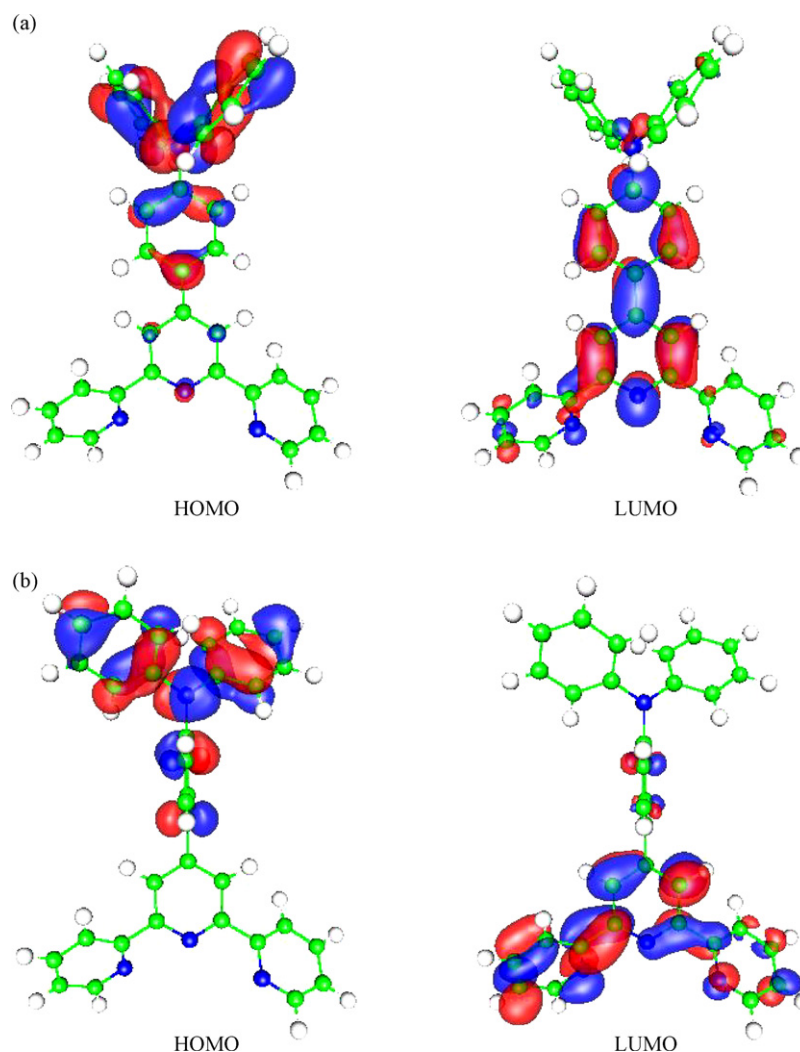


Fig. 5. Frontier molecular orbitals (MOs) of the DPAPT molecule at the geometry of the LE excited state (a) and of the twisted ICT excited state (b).

has a minimum at 10° and 90° of the S_1 and S_2 states, respectively, with an intersection of the S_1 (LE) and S_2 (ICT) states at ca. 60° (see Fig. 4b). The potential energy curves imply a relatively weak barrier for twisting both the angle φ and θ in the excited state. After photoexcitation, DPAPT can be initially excited to the unrelaxed S_1 state (Fig. 5a), and in succession the diphenylamino and triphenylamine group wag along the N(32)–C(22) and C(19)–C(11) bond, respectively, until it gets a stable conformational geometry with the completely charge transfer from donor to acceptor (see Fig. 5b) [10]. The possibility of an energetic minimum is proposed because of the nearly complete orbital decoupling at the twisting geometry leading to the bi-radical character of the corresponding excited state, if the interaction with the other states (e.g., of mesomeric character) is not strong [18]. In polar solutions, the configuration with the maximum dipole moment is preferentially stabilized, so that for strong dipolar stabilization and weak mesomeric interaction, the lowest excited state corresponds to the twisted structure [41], considering the result of the potential energy curves. Therefore the fluorescence is preferentially emitted from the state where angles of the diphenylamino and triphenylamine group are both twisted. The formation of ICT for DPAPT should be reasonably accompanied by a relaxation to the TICT state.

In addition, the LE and ICT character of the excited states can also be clearly confirmed from the frontier molecular orbital (MO) calculations of the DPAPT, which are shown in Fig. 5. By fixing the φ angle at 60° as it is the minimum of its relevant PES (Fig. 4a),

the calculation of the vertical excitation energies of the molecule with the θ angle at 10° (LE) and 90° (ICT) (Fig. 4b) are performed. It can be seen clearly from Fig. 5a and b that the electron density of HOMO is localized in the triphenylamine group, while the population of the LUMO makes a crucial difference between LE and ICT structures. When the θ angle is 10° , the localization of this orbit is mainly in the benzene ring which is attached to the diphenylamino and tpy and displays a LE character; whereas, when the θ angle is 90° , the electron density almost localizes on the acceptor (tpy) group entirely, indicating a completely charge transfer from donor to acceptor [11,12].

4. Conclusion

In summary, we have experimentally and theoretically investigated the photophysics and relaxation dynamics of the singlet excited state of DPAPT. Large Stokes shift in more polar solvents suggest the ICT character of the excited state at room temperature. The $\Delta\mu$ were determined by using the Lippert–Mataga equation, and the absolute value of $\Delta\mu$ is calculated to be 13.66 D, which is larger as compared to the ground state ($\mu_g = 3.99$ D), in accordance with the fluorescence measurements.

As far as we know, for the majority of the simple organic D–A molecules, the charge separation is more favorable in a twisted conformation. As a possible explanation, twisting intramolecular charge transfer has been employed to analyze the conformational

relaxation of DPAPT. That is, the photoexcited DPAPT can be initially excited to the unrelaxed S_1 state, and in succession an intramolecular charge transfer takes place accompanying the diphenylamino and triphenylamine group wag until it attains the most stable conformational geometry. According to our theoretical studies, the potential energy curve as a function of twisting angle θ and φ indicates that the stable conformational geometry of the excited state differentiates it from that of the ground state, which has minimum energy around $10^\circ/90^\circ$ and 60° relative to twisting of θ and φ , respectively.

As a general result for the DPAPT, it is concluded that the excited state has a twisted intramolecular charge transfer character, which displays strong fluorescent emission. More theoretical and experimental studies of the twisting dynamics on terpyridine compound are required.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (Grants 20633070 and 20833008), the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant DICP K2007/F2), and NKBRFSF (Grants 2007CB815202 and 2009CB220010).

References

- [1] W.L.E. Lippert, F. Moll, W. Nägele, H. Boos, H. Prigge, I. Seibold-Blankenstein, *Angew. Chem.* 73 (1961) 695–706.
- [2] W. Rettig, *Angew. Chem. Int. Ed.* 25 (1986) 971–988.
- [3] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.* 103 (2003) 3899–4031.
- [4] J. Dobkowski, J. Wojcik, W. Kozminski, R. Kolos, J. Waluk, J. Michl, *J. Am. Chem. Soc.* 124 (2002) 2406–2407.
- [5] B. Mennucci, A. Toniolo, J. Tomasi, *J. Am. Chem. Soc.* 122 (2000) 10621–10630.
- [6] C.J. Jodice, H.P. Luthi, *J. Am. Chem. Soc.* 125 (2003) 252–264.
- [7] Y.V. Il'ichev, W. Kuhnle, K.A. Zachariasse, *J. Phys. Chem. A* 102 (1998) 5670–5680.
- [8] J.S. Yang, K.L. Liau, C.M. Wang, C.Y. Hwang, *J. Am. Chem. Soc.* 126 (2004) 12325–12335.
- [9] J.S. Yang, S.Y. Chiou, K.L. Liau, *J. Am. Chem. Soc.* 124 (2002) 2518–2527.
- [10] W. Schuddeboom, S.A. Jonker, J.M. Warman, U. Leinhos, W. Kuhnle, K.A. Zachariasse, *J. Phys. Chem.* 96 (1992) 10809–10819.
- [11] A. Kohn, C. Hattig, *J. Am. Chem. Soc.* 126 (2004) 7399–7410.
- [12] D. Rappoport, F. Furche, *J. Am. Chem. Soc.* 126 (2004) 1277–1284.
- [13] S. Wilsey, K.N. Houk, A.H. Zewail, *J. Am. Chem. Soc.* 121 (1999) 5772–5786.
- [14] F. Lahmani, A. Zehnacker-Rentien, L.H. Coudert, K.A. Zachariasse, *J. Phys. Chem. A* 107 (2003) 7364–7372.
- [15] K. Seo, A.V. Konchenko, J. Lee, G.S. Bang, H. Lee, *J. Am. Chem. Soc.* 130 (2008) 2553–2559.
- [16] D.L. Ma, C.M. Che, S.C. Yan, *J. Am. Chem. Soc.* 131 (2009) 1835–1846.
- [17] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Pechy, M. Graetzel, *Chem. Commun.* (2008) 5194–5196.
- [18] K. Senecal-David, A. Hemeryck, N. Tancrez, L. Toupet, J.A.G. Williams, I. Ledoux, J. Zyss, A. Boucekkinne, J.P. Guegan, H. Le Bozec, O. Maury, *J. Am. Chem. Soc.* 128 (2006) 12243–12255.
- [19] T. Akasaka, J. Otsuki, K. Araki, *Chem. Eur. J.* 8 (2002) 130–136.
- [20] L. De Cola, P. Belsler, *Coord. Chem. Rev.* 177 (1998) 301–346.
- [21] W. Goodall, K. Wild, K.J. Arm, J.A.G. Williams, *J. Chem. Soc.: Perkin Trans. 2* (2002) 1669–1681.
- [22] A.M.W. Cargill Thompson, *Coord. Chem. Rev.* 160 (1997) 1–52.
- [23] G. Albano, V. Balzani, E.C. Constable, M. Maestri, D.R. Smith, *Inorg. Chim. Acta* 277 (1998) 225–231.
- [24] J.C. Loren, J.S. Siegel, *Angew. Chem. Int. Ed.* 40 (2001) 754–757.
- [25] C.J. Aspley, J.A.G. Williams, *New J. Chem.* 25 (2001) 1136–1147.
- [26] W. Goodall, J.A.G. Williams, *Chem. Commun.* (2001) 2514–2515.
- [27] R. Ahlrichs, M. Bar, M. Haser, H. Horn, C. Kolmel, *Chem. Phys. Lett.* 162 (1989) 165–169.
- [28] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [29] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* 102 (1995) 346–354.
- [30] A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 100 (1994) 5829–5835.
- [31] G.-J. Zhao, K.-L. Han, *J. Phys. Chem. A* 111 (2007) 2469–2474.
- [32] A.M. Brun, A. Harriman, Y. Tsuboi, T. Okada, N. Mataga, *J. Chem. Soc.: Faraday Trans.* 91 (1995) 4047–4057.
- [33] E. Lippert, *Z. Naturforsch., Phys. Sci. A* 10 (1955) 541–545.
- [34] Y.V. Il'ichev, W. Kuhnle, K.A. Zachariasse, *Chem. Phys.* 211 (1996) 441–453.
- [35] W. Baumann, H. Bischof, J.C. Fröhling, C. Brittinger, W. Rettig, K. Rotkiewicz, *J. Photochem. Photobiol. A* 64 (1992) 49–72.
- [36] J.T. Edward, *J. Chem. Educ.* 47 (1970) 261–269.
- [37] G.J. Zhao, R.K. Chen, M.T. Sun, J.Y. Liu, G.Y. Li, Y.L. Gao, K.L. Han, X.C. Yang, L. Sun, *Chem. Eur. J.* 14 (2008) 6935–6947.
- [38] M. Liang, W. Xu, F.S. Cai, P.Q. Chen, B. Peng, J. Chen, Z.M. Li, *J. Phys. Chem. C* 111 (2007) 4465–4472.
- [39] W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, *J. Phys. Chem. C* 112 (2008) 874–880.
- [40] T. Mutai, S. Arita, K. Araki, *J. Chem. Soc.: Perkin Trans. 2* (2001) 1045–1050.
- [41] W. Rettig, M. Maus, *Conformational Analysis of Molecules*, in: J. Waluk (Ed.), *Excited States*, New York, Wiley-VCH, 2000, Ch. 1, pp. 1–55.