# Photoinduced Coupled Charge and Proton Transfers in Gradually Twisted Phenol-Pyridinium Biaryl Series

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A detailed photophysical analysis of a phenol-pyridinium biphenyl series with gradual twisted geometry is presented in this paper. The low-energy CT absorption band of the compounds undergoes a decrease of intensity with a progressive blue shift by increasing the twist angle of the central bond ( $\Theta_{AD}$ ). These effects are well described and quantified within the framework of the Mulliken-Murrel approach, which allows us to extend such a model to the charge-shift process. The biaryl compounds exhibit broadened fluorescence bands assigned to the radiative deactivation of a charge shift (CSh) species generated by an intramolecular twisting relaxation of the locally excited (LE) state. Parallel to the rotamerism of the central single bond, excited-state proton-transfer (ESPT) processes are occurring from both excited states and lead to the nonemissive phenolate forms. Solvatochromic shifts of the emission bands are correlated by the Kamlet-Taft parameters  $(\pi^*, \alpha, \text{ and } \beta)$ . The correlation first confirms the  $\pi^*$  dependence of the CSh band shift but also demonstrates a clear  $\beta$  dependence. The contribution of the latter parameter to the band hypsochromy is markedly increasing with  $\Theta_{AD}$ . Such an unusual effect was ascribed to a much higher ESPT rate relative to the highly twisted conformation with respect to that of more planar geometry. Despite the suppression of the geometrical relaxation in ethanol glass at 77 K, the fluorescence of the phenolate species produced by ESPT from LE state is detected. The relative increase of its fluorescence band intensity with  $\Theta_{AD}$  confirms the gradual enhancement of the excited states acidity.

#### 1. Introduction

Addressing the factors that mainly impact the photoinduced intramolecular charge-transfer (ICT) process constitutes an appealing challenge for the development of molecular devices devoted to a large set of applications in solar energy conversion, artificial photosynthetic systems,<sup>1</sup> chemosensors,<sup>2</sup> high-performance optoelectronic materials, and proton photorelease systems.<sup>3,4</sup> For this purpose, several key parameters can be methodically modulated on the basis of relevant series of donor-acceptor models: (i) the nature of the donor and acceptor subunits which thermodynamically allow the photoinduced ICT<sup>5,6</sup> process, (ii) the nature and the length of the linker which ensures either the charge delocalization or confinement,<sup>7-10</sup> and (iii) the amplitude of the relative motion between each donor and acceptor subunit at excited states.<sup>11,12</sup> In connection with this latter factor, the 4-(dimethylamino)benzonitrile<sup>13-17</sup> has been extensively studied as a reference example. This simple donor-acceptor molecule exhibits a dual fluorescence emission in a polar medium. The proposed model, which has been the source of controversial discussions for more than 20 years,<sup>18–20</sup> relates a photoinduced ICT process from the amino group to the benzonitrile moiety with a concomitant rotation between both subunits. Hence the new fluorescence band stems from the radiative deactivation of a twisted internal charge-transfer species (TICT). Such a model has been generalized for larger conjugated  $\pi$ -systems<sup>11</sup> or for donor-acceptor biaryl models.<sup>15,21-24</sup> The possibility of conformational twist in the excited state is mainly dependent on the energetic barrier between the locally excited and the charge-transfer state. Ultimately, this barrier, which is strongly influenced by the donor or acceptor nature, can be suppressed,<sup>23</sup> as observed for dimethylanilino- or thiophenopyridinum derivatives.<sup>23,25-27</sup> The large electron affinity of pyridinium group ( $E_{\rm red} = -1.21 \text{ eV}^7$ ) is assumed to be responsible for this dramatic effect. Therefore, integrated in D-A biaryl systems, the pyridinium moiety constitutes an interesting candidate that should both promote a  $\pi$ -conjugated planar conformation in the ground state and lead to a large amplitude twisting relaxation in the excited state. By association with a proton donor group, a coupling with an excited-state proton-transfer (ESPT) process can be observed. The strategy that consists of enhancing the excited-state acidity due to the effect of a primary photoinduced ICT is well established for rigid hydroxyarenes such as 2-naphthol,<sup>28-33</sup> pyranine,<sup>34-37</sup> and 6-hydroxyquinoline<sup>38,39</sup> derivatives. The role of the withdrawing substituent<sup>40,41</sup> coupled with the polarization of the electronic transition<sup>42</sup> was empha-

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SCHEME 1: Molecular Structures of Biphenyl Derivatives (PhPy1 to PhPy4)



sized to trigger the excited-state acidity. Moreover, it was demonstrated that the solvation of the anionic conjugated base, which is subsequently produced, largely contributes to the exothermy of ESPT.<sup>30,43</sup> However, to our knowledge, few examples<sup>44</sup> were proposed to extend the investigation to systems that correlate ESPT to conformational change.

In the present paper we describe a detailed photophysical analysis of a phenol-pyridinium biaryl series where the twist angle relative to the aryl-aryl bond is gradually increased by sterically hindering substituents (Scheme 1). Such a conformation modulation has strong consequences at ground and excited states.

#### 2. Experimental Section

**2.1. Compounds.** Compounds PhPy1 to PhPy4, twisted by introduction of crowded alkyl groups on the pyridine ring, are obtained by protonation of their corresponding zwitterion forms whose synthesis and characterization are detailed elsewhere.<sup>45,46</sup> The addition of stoichiometric amount of trifluoroacetic acid leads to the quantitative formation of the phenol form. The complete protonation of each chromophore was indeed checked upon the total disappearance of the last absorption band of the zwitterion.<sup>47</sup> Hence, the counterion of the cationic chromophores is CF<sub>3</sub>COO<sup>-</sup>. The presence of the crowded *tert*-butyl substituents in ortho positions of the phenol group prevents self-aggregation, which was confirmed by checking the Beer–Lambert law in the millimolar concentration range.

**2.2. Solvents.** The solvents used for absorption and emission analysis are as follows: butyl ether (BOE), ethyl ether (EOE), butyl acetate (BuAc), ethyl acetate (EtAc), butyl chloride (nBuCl), tetrahydrofuran (THF), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), propionitrile (PPCN), acetonitrile (ACN), ethanol (EtOH), methanol (MeOH), 2-propanol (2-propanol), trifluoroethanol (TFE). All the solvents employed were Aldrich or Fluka spectroscopic grade. The absorption and fluorescence of all solvents were checked for impurities and have been subtracted from the sample spectra.

**2.3. Instrumentation and Procedures.** The absorption measurements were carried out with a Perkin-Elmer Lambda 2 spectrometer. A FluoroMax-4 spectrofluorometer was used for the fluorescence and phosphorescence measurements. All emission spectra were corrected for instrumental response and were converted from the recorded wavelength scale  $I_f(\lambda_f)$  to a linear energy scale according to the relationship  $I_f(\nu_f) = I_f(\lambda_f) \times \lambda_f^2$ . The fluorescence quantum yields include the correction due to solvent refractive index and were determined relative to quinine



Figure 1. Absorption spectra of biaryl derivatives (solvent: acetonitrile).

bisulfate in 0.05 molar sulfuric acid ( $\Phi_f = 0.52$ ).<sup>48</sup> The fluorescence quantum yields were obtained from five independent measurements, and the uncertainties were determined to  $\pm 10\%$  for 0.2 >  $\Phi_f$  > 0.02 and  $\pm 20\%$  for 0.02 >  $\Phi_f$  > 5 × 10<sup>-3</sup>.

Phosphorescence and steady-state anisotropy measurements were performed in ethanol at 77 K. The samples are placed in a 5 mm diameter quartz tube inside a Dewar filled with liquid nitrogen. Two Glan-Thompson polarizers are placed in the excitation and emission beams. The anisotropy *r* is determined as follows:  $r = (I_{VV} - gI_{VH})/(I_{VV} + 2gI_{VH})$  with  $g = I_{HV}/I_{HH}$ , where *I* is the fluorescence intensity. The subscripts denote the orientation (horizontal H or vertical V) of the excitation and emission polarizers, respectively. *g* is an instrumental correction factor. The proper calibration of the setup was checked using a recent standard method with rhodamine 101 in glycerol.<sup>49</sup>

Fluorescence lifetimes were obtained using a Nano LED emitting at 344 nm as an excitation source with a nano led controller module, Fluorohub from IBH, operating at 1 MHz. The detection was based on a R928P type photomultiplier from Hamamatsu with a high-sensitivity photon-counting mode. The decays were fitted with the iterative reconvolution method on the basis of the Marquardt–Levenberg algorithm.<sup>50</sup> Such a reconvolution technique<sup>51</sup> allows an overall-time resolution down to 0.2 ns. The quality of the exponential fits was checked using the reduced  $\chi^2$  ( $\leq 1.2$ ).

Semiempirical quantum chemical calculations were performed using AM1 method (from HYPERCHEM package<sup>52</sup>).

### 3. Results and Discussion

**3.1.** Absorption and Emission Spectra in Acetonitrile. Room temperature absorption bands and fluorescence spectra of compounds are illustrated in Figures 1 and 2. Absorption and emission data are collected in Tables 1–3. The red-energy side of the absorption spectrum exhibits a distinctive structureless band that is blue-shifted from PhPy1 to PhPy4. This band shows a concomitant decrease of its intensity that is divided by a factor 10 (Table 2). By analogy with D–A biphenyls previously studied,<sup>21,53–55</sup> this well separated band can be ascribed to the <sup>1</sup>CT  $\leftarrow$  S<sub>0</sub> transition from the phenol fragment to the pyridinium one. The steady-state excitation anisotropy spectra depicted in Figure 3 confirm the existence of this transition: For all chromophores, the anisotropy spectrum clearly



Figure 2. Normalized fluorescence spectra of biaryl derivatives in ethyl ether, ethyl acetate, and acetonitrile (from left to right, respectively).

displays a plateau below 33 000 cm<sup>-1</sup> with constant values of  $0.34 \pm 0.01, 0.35 \pm 0.01, 0.35 \pm 0.02$ , and  $0.37 \pm 0.02$  for PhPy1 to PhPy4, respectively. Moreover, in the high-energy side of the spectrum, the anisotropy decreases and reaches another plateau in the 36 000-37 500 cm<sup>-1</sup> region, indicating the presence of an other transition. This transition can be assigned to the  ${}^{1}L_{a} \leftarrow S_{0}$  one corresponding to the A band located around 36 500 cm<sup>-1</sup> in acetonitrile. In the same manner, the B band observed in the high-energy part of the absorption spectrum (Figure 1) can be assigned to the  ${}^{1}B_{b} \leftarrow S_{0}$  transition. Interestingly, the progressive alkylation of the pyridinium moiety leads to a red-shift of this B band and suggests that the transition involves molecular orbitals centered on the pyridinium subunit. A detailed comparison of the absorption spectra for each compound shows that the decrease of the  ${}^{1}CT \leftarrow S_{0}$  band is related to a slight growth of the  ${}^{1}L_{a} \leftarrow S_{0}$  one. This effect illustrates a possible electronic coupling of the <sup>1</sup>L<sub>a</sub> state with the low lying <sup>1</sup>CT state, which exhibits the same <sup>1</sup>A symmetry. The electronic transition dipole moments can be used to quantify the electronic coupling between the  ${}^{1}CT$  and S<sub>0</sub> states in the framework of Mulliken's two-state model<sup>56</sup> or between the <sup>1</sup>CT and close lying <sup>1</sup>LE state with the same symmetry according the intensity "borrowing" concept proposed by Murell.<sup>57</sup> Moreover, the electronic transition moment relative to the CT state constitutes a suitable variable to derive information about the change of the twist angle  $\Theta_{A-D}$  between the ground and excited state. The transition dipole moment  $M_{\rm abs}$ relative to the  ${}^{1}CT \leftarrow S_{0}$  absorption can be calculated according to the expression58,59

$$M_{\rm abs}^{2} = \frac{3hc10^{3}\ln 10}{8\pi^{3}N_{\rm A}n} \int \varepsilon(\nu_{\rm A}) \,\mathrm{d}(\ln\nu_{\rm A}) \tag{1}$$

where  $\varepsilon(\nu_A)$  corresponds to the molar extinction coefficient of the CT band at wavenumber  $\nu_A$ ; *n*, *h*, *c*, and  $N_A$  are the refractive index of the solvent, the Planck constant, the speed of light, and the Avogadro number, respectively. The transition moments are collected in Table 2. We can clearly notice that the transition moment decreases from PhPy1 to PhPy4. If we assume that the value of the transition dipole moments are provided from two main components (the transition dipole moment of the <sup>1</sup>L<sub>a</sub> ← S<sub>0</sub> ( $M_{1La}$ ) and the contribution stemming from the direct interaction between the <sup>1</sup>CT state and the ground state), the transition moment can be expressed as follows:<sup>60</sup>

$$M_{\rm abs} \approx c_1 \frac{V_0(\mu_{\rm e} - \mu_{\rm g})}{hc\nu_{\rm abs}^{\rm CT}} + c_2 M_{\rm 1La}$$

$$c_1^2 + c_2^2 = 1$$
(2)

The first term of this approximation corresponds to the Mulliken two-state model<sup>56</sup> where  $(\mu_e - \mu_g)$  denotes the difference of dipole moments between ground and excited states.  $V_0$  corresponds to the electronic coupling element between the <sup>1</sup>CT state and the ground state. According to Dogonadze et al.,<sup>61</sup>  $V_0$  can be determined by the interactions between the carbons atoms forming the A–D bond as

$$V_0 = c_{\rm D} c_{\rm A} \beta_{\rm DA} \cos \Theta_{\rm AD} \tag{3}$$

where  $\Theta_{AD}$  is the twist angle between the planes of the acceptor and donor fragments,  $\beta_{AD}$  is the resonance integral of the two neighboring carbon atoms ( $\beta_{AD} = -2.39$  eV for benzene carbon atoms<sup>62,63</sup>),  $c_{\rm D}$  and  $c_{\rm A}$  are the LCAO coefficients of the p $\pi$  atomic orbital relative to the HOMO and LUMO respectively. These latter coefficients can be obtained by the AM1 method. With AM1  $c_D$  and  $c_A$  coefficients (0.46 and 0.56 as calculated for isolated 2,5-di-tert-butylphenol and N-methylpyridinium chromophores), one can estimate  $V_0$  coupling constants ranging from ca. 0.29 eV for PhPy4 to ca. 0.55 for PhPy1 compounds (see Table 2). The estimated  $V_0$  allow prediction of transition dipole moments  $M_{abs}$  by taking into account <sup>1</sup>CT  $\leftarrow$  S<sub>0</sub> transition energies and differences between  $\mu_{e}$  and  $\mu_{g}$  dipole moments. In the case of the investigated species, electron transfer takes place from the phenolic oxygen to the nitrogen atom of the Nmethylpyridinium kernel with a charge-shift distance of ca. 6-8Å and  $\mu_e - \mu_g$  difference as high as 30–40 D, correspondingly. Using the first right-hand term of relation 2 ( $c_1 \sim 1$ ), one can finally calculate  $M_{abs}$  expected values as collected in Table 2 (estimated with  $\mu_e - \mu_g = 35$  D). From the plot of  $M_{abs}$  vs  $M_{\rm abs}^{\rm cal}$  a very good linear correlation is obtained for all

TABLE 1: Spectroscopic Data of PhPy 1–4 at Room Temperature in Various Solvents: Absorption and Fluorescence Transition Energy Maxima, Stocks Shifts, and Band Half-Widths (All in cm<sup>-1</sup>)

no.	solvent	$\nu_a^{max}$	$ u_{\rm f}^{\rm max}$	$\Delta \nu_{ m ST}$	$HW_a$	$HW_{\rm f}$		
PhPy1								
1	BOB	28650	24040	4610	3670	4070		
2	EOE	28740	23920	4820	3810	3810		
3	BuAc	29030	23360	5670	4230	3860		
4	EtAc	28990	23150	5840	4030	3920		
5	THE	28330	23090	5240	4080	3860		
6	CH <sub>2</sub> Cl <sub>2</sub>	26740	22990	3750	3240	3760		
7	PPCN	28900	22270	6630	3860	4200		
8	ACN	28000	22270	6770	4030	4310		
0	MaOH	20990	22220	4020	4200	4070		
9	EtOU	20410	23430	4960	4290	4070		
10	EIOH	28170	23830	4340	4150	3070		
11	2-propanol	28090	23840	4250	4220	3300		
12	IFE	27930	22190	5/40	3/40	4570		
13	nBuCl	27930	22830	5100	3600	3870		
			PhPy2	< <b>7.9</b> .0		52.40		
1	ROR	29590	23070	6520	4170	5340		
2	EOE	29850	22620	7230	4430	4990		
3	BuAc	30030	21600	8430	4560	5060		
4	EtAc	30030	21360	8670	4640	4960		
5	THF	29410	21350	8060	4530	4940		
6	$CH_2Cl_2$	27550	21690	5860	4030	4110		
7	PPCN	29760	19760	10000	4450	4760		
8	ACN	29940	19760	10180	4530	4730		
9	MeOH	29500	22970	6530	4760	5140		
10	FtOH	29070	23640	5430	4720	4940		
11	2-propanol	28900	24000	4900	4730	4750		
12	2-propanoi	28900	24000	9100	4240	4730		
12	IFE "DuCl	20370	20390	0190 7640	4340	4040		
15	IIBUCI	28740	21100	/640	4170	4910		
1	DOD	20400	PhPy3	0.400	4790	5520		
1	BOB	30400	21980	8420	4/80	5530		
2	EOE	30770	21980	8790	4960	5180		
3	BuAc	30680	20920	9750	5100	4970		
4	EtAc	30770	20410	10360	5260	4820		
5	THF	29940	20490	9450	5120	5010		
6	$CH_2Cl_2$	28010	21410	6600	4330	4030		
7	PPCN	30400	19310	11090	4700	4410		
8	ACN	30770	19190	11580	5180	4360		
9	MeOH	30210	22570	7640	5290	6270		
10	EtOH	30030	23250	6780	5300	5320		
11	2-propanol	29500	23830	5670	5290	4370		
12	TFE	29410	20080	9330	4800	4390		
13	nBuCl	29670	20880	8800	4530	4620		
			DhDv/					
1	BOB	31060	22580	8480	5750	5030		
2	FOF	31300	22360	0050	5500	4810		
2	EUE Du A a	21450	21210	10220	5410	4010		
3	BUAC	21450	21210	10230	5410	4700		
4	EIAC	31450	20760	10090	5820	4/00		
2	THE	30080	20080	9990	5770	4080		
6	$CH_2Cl_2$	28490	21460	7030	4800	4090		
7	PPCN	30860	19460	11410	5250	4410		
8	ACN	31250	19280	11970	5550	4320		
9	MeOH	30770	21290	9480	5840	5270		
10	EtOH	30400	23090	7310	5740	6720		
11	2-propanol	30120	23730	6390	5610	5100		
12	TFE	29500	20260	9240	4940	4340		
13	nBuCl	30210	20870	9340	4940	4540		

compounds (Figure 4). This agreement suggests that one can neglect the contribution from mixing of the  ${}^{1}L_{a}$  and  ${}^{1}CT$  states in all investigated molecules. A similar conclusion can be drawn by comparing energies of the excited  ${}^{1}CT$  states calculated from absorption and emission data. Nearly the same  $(hcv_{flu} + hcv_{abs})/2$ values (e.g.,  $3.12 \pm 0.05$  eV in acetonitrile solutions) are characteristic for all four of investigated compounds, as could be expected by assuming only the sterical effect of alkyl group(s)

 TABLE 2: Room Temperature Absorption Data for Biaryl

 Compounds in Acetonitrile: Experimental and Calculated

 Values of the Absorption Transition Dipole Moments

	$\epsilon (\nu_{abs}^{CT})^a$	$\nu_{abs}^{{ m CT},b}~{ m eV}$	$\begin{array}{c} \Theta_{\text{A-D}},\\ \text{deg} \end{array}$	V <sub>0</sub> , eV	$\stackrel{M_{abs}^{\ \ cal,}}{\mathrm{D}}$	$M_{abs}, D^c$
PhPy1	26400	3.60	28.3	0.55	5.3	5.8
PhPy2	14700	3.71	43.7	0.46	4.3	4.7
PhPy3	5600	3.82	53.6	0.39	3.6	3.0
PhPy4	2600	3.88	65.5	0.29	2.6	2.0

<sup>*a*</sup> Error is about: 5-10%. <sup>*b*</sup> Scatter of results:  $\pm 0.01$  eV. <sup>*c*</sup> Experimental error: 0.1 - 0.2 D.

TABLE 3: Solvent Effect on the Fluorescence QuantumYields, Decay Times, and Resulting Radiationless andRadiative Rate Constants, and Electronic Transition DipoleMoments of Biaryl Derivatives

J	1	Ф		$k_{\rm nr} \propto 10^7$	$k_{\rm f} \times 10^{7}$	$M_{\rm flu}$
compa	solvent	$\Psi_{\mathrm{f}}$	$\tau$ , ns	s -	S ·	D
PhPy1	EOE	0.016	< 0.2			
	$CH_2Cl_2$	0.47	5.1	10.4	9.2	2.1
	PPCN	0.13	1.7	51.2	7.6	2.1
	ACN	0.11	1.6	55.6	6.9	2.1
	EtOH	< 0.001	< 0.2			
	TFE	0.14	1.5	57.3	9.3	2.6
PhPy2	EOE	0.007	< 0.2			
	$CH_2Cl_2$	0.28	10.3	7.0	2.7	1.2
	PPCN	0.051	2.1	45.2	2.4	1.4
	ACN	0.034	2.0	48.3	1.7	1.2
	EtOH	< 0.001	< 0.2			
	TFE	0.042	1.6	59.9	2.6	1.5
PhPy3	EOE	0.004	< 0.2			
	$CH_2Cl_2$	0.19	13.7	5.9	1.4	0.9
	PPCN	0.034	3.0	32.2	1.1	1.0
	ACN	0.020	2.6	37.7	0.8	0.9
	EtOH	< 0.001	< 0.2			
	TFE	0.028	1.9	51.2	1.5	1.2
PhPy4	EOE	0.003	< 0.2			
	$CH_2Cl_2$	0.20	17.3	4.6	1.2	0.8
	PPCN	0.032	4.0	24.2	0.8	0.8
	ACN	0.020	3.7	26.5	0.5	0.7
	EtOH	< 0.001	< 0.2			
	TFE	0.031	2.5	38.8	1.2	1.1

attached to the pyridinium ring. The stronger the interaction between <sup>1</sup>CT and <sup>1</sup>L<sub>a</sub> states, the lower is energy of the <sup>1</sup>CT state and the lower is value of  $(hcv_{flu} + hcv_{abs})/2$ , respectively. If the



**Figure 3.** Excitation anisotropies of D–A biphenyls in glassy matrix of ethanol at 77 K ( $\nu_{em}$ : 24 690 cm<sup>-1</sup>): PhPy1 (squares), PhPy2 (circles), PhPy3 (triangle), PhPy4 (diamond).



Figure 4. Correlation between experimental and calculated values of the absorption transition dipole moments.

<sup>1</sup>CT state would strongly interact with the <sup>1</sup>L<sub>a</sub> state, one could expect well pronounced changes in  $(hc\nu_{flu} + hc\nu_{abs})/2$  as well.

Protolytic properties of the chromophores are also strongly influenced by pretwisting. The  $pK_a$  relative to the phenolate phenol equilibrium was determined by the spectrophotometric method upon addition of CF<sub>3</sub>COOH to solutions of acetonitrile with the corresponding zwitterion. The  $pK_a$  gradually increases from a value of ca. 9.10 for PhPy1 to 12.70 for PhPy4. This tendency is clearly assigned to a charge-transfer enhancement from the phenol group to the pyridinium one. In the excited state, such an effect will be investigated hereafter.

The fluorescence spectrum in acetonitrile consists of a structureless band that is red-shifted and broadens out from PhPy1 to PhPy4 (Figure 2). The Stokes shift is markedly increasing with a value of ca. 6770 cm<sup>-1</sup> for PhPy1 to a larger one of ca. 11 970 cm<sup>-1</sup> for PhPy4. This hints at a significant electronic and/or geometrical change between the ground and excited state. For such ionic compounds, fluorescence can be attributed to a relaxed charge transfer or more precisely charge shift state23,25-27,54,64 (CSh) that is connected to a twisted geometry. Figure 5 shows the fluorescence decays of compounds in acetonitrile. It should be stressed that, under our time resolution, decays are monoexponential at all monitoring wavelengths and do not contain any contribution of long-lived component. From a first approximation, if we assume an irreversible charge shift state formation, the radiative and radiationless rate constant can be determined as follows:

$$k_{\rm f} = \frac{\Phi_{\rm f}}{\tau} \tag{4}$$

$$k_{\rm nr} = \frac{(1 - \Phi_{\rm f})}{\tau} \tag{5}$$

The experimental values of  $k_{\rm f}$  show a significative decrease from ca.  $6.9 \times 10^7 \,{\rm s}^{-1}$  for PhPy1 to ca.  $0.5 \times 10^7 \,{\rm s}^{-1}$  for PhPy4 (Table 3). Hence, sterically hindered derivatives acquire a forbidden emissive character in accordance with the population of highly twisted conformation. Interestingly, a methodical increase of  $k_{\rm nr}$  is observed by releasing sterical restriction around the central single bond, this should be ascribed to a much larger amplitude relaxation toward the twisted geometry. The electronic transition dipole moments  $M_{\rm f}$  are calculated according to the expression<sup>65</sup>

$$k_{\rm f} = \frac{64\pi^4}{3h} n^3 v_{\rm f}^{\ 3} M_{\rm f}^{\ 2} \tag{6}$$

The significant differences between  $M_{\rm f}$  and  $M_{\rm abs}$  values (Tables 2 and 3) confirm the strong electronic and geometrical relaxation in the excited states. By analogy with (dimethylanilino)pyridinium derivatives that have been mainly described by Fromherz et al.,53,54,64 a precursor-successor model can be proposed to account this photophysical behavior. The model involves dual fluorescence from a locally excited (LE) species (resonance-type state stabilized by mesomeric interaction) and a successor charge shift (CSh) species with twisted geometry. Rettig et al.<sup>25,26</sup> clearly demonstrated from quantum calculations that the ionic D-A biphenyls undergo an energetic barrierless twist relaxation toward the 90° energetic minimum with charge shift whereas the neutral donor-acceptor biphenyls exhibit a sizable rotation barrier in the  $S_1$  surface. Moreover, a subsequent equilibration of the two excited states can be observed. This rapid thermal equilibration between LE and CSh states was observed for the 9-mesityl-10-methylacridinium cation<sup>66</sup> for instance. In our case, thermal equilibration is also demonstrated through a temperature dependence analysis. Figure 6 displays the evolution of emission spectra of PhPy1 and PhPy4 in acetonitrile upon an increase in temperature over the range 5-80 °C. The emission band of PhPy1 decreases monotonically without spectral shift whereas the fluorescence decrease for PhPy4 is accompanied by a band blue shift. The proximity in energy of LE and CSh states should promote a thermal population of a high lying LE state from the relaxed CSh one; the relative ratio for the radiative rate constants can be well described in terms of the Boltzmann expression with an energy gap decreasing from ca. 7.5  $\pm$  0.2 kJ mol^{-1} for PhPy1 to ca.  $4.4 \pm 0.2$  kJ mol<sup>-1</sup> for PhPy4. From PhPy1 to PhPy4, the decrease of the energy gap between the LE and CSh states is in line with their increasing geometrical equivalency due to the additional help of pretwisting.

**3.2.** Analysis of the Solvent Induced Spectral Shift. Solvent effects on the absorption bands do not follow the classical Lippert–Mataga<sup>67,68</sup> behavior. Despite a significant change of the dipole moment upon excitation, the CT absorption band seems slightly sensitive to solvent polarity. This suggests that specific solute–solvent interactions are not negligible in the ground state. At the S<sub>1</sub> state, the dipole–dipole interactions become significant since better correlations can be derived.

Therefore, to rationalize all the solute—solvent interactions at both the ground and excited states, we use the empirical Kamlet—Taft solvatochromic parameters:<sup>69,70</sup>  $\pi^*$ ,  $\alpha$ , and  $\beta$ . The values of solvent parameters are collected in Table 4. Parameter  $\pi^*$  is a measure of the nonspecific solvent polarity/polarizability, whereas  $\alpha$  and  $\beta$  indicate the solvent hydrogen bond (HB) donating and accepting properties. The spectral shift can therefore be linearly correlated with these parameters by

$$\nu = \nu_0 + p\pi^* + a\alpha + b\beta \tag{7}$$

Coefficients p, a, and b are related to solute properties: p refers to the solute dipole moment, a evaluates its ability to donate a HB to the solvent, b measures the tendency of the solute to accept a HB from the solvent. Excluding haloaliphatic solvents which deviate from correlation, multilinear regressions to the absorption and emission data lead to coefficients listed in Table 5. Figure 7 displays the correlation between the calculated maxima of fluorescence as a function of the experimental values in various solvents.



Figure 5. (a) Time fluorescence decay of biaryl derivatives in acetonitrile; instrumental response function (IRF). (B) Residual graphs relative to monoexponential fits.



Figure 6. Temperature effect on the fluorescence spectra of PhPy1 (A) and PhPy4 (B). Inset: Arrhenius plot for the emission quantum yield (solvent: acetonitrile).

 TABLE 4: Values of Kamlet and Taft Parameters of Various Solvents

no.	solvent	$\pi^*$	α	β
1	BOB	0.18	0	0.46
2	EOE	0.27	0	0.47
3	BuAc	0.51	0.06	0.45
4	EtAc	0.55	0.06	0.45
5	THF	0.58	0	0.55
6	$CH_2Cl_2$	0.82	0.30	0.10
7	PPCN	0.64	0	0.37
8	ACN	0.75	0.19	0.40
9	MeOH	0.60	0.98	0.66
10	EtOH	0.54	0.86	0.75
11	2-propanol	0.48	0.76	0.90
12	TFE	0.73	1.51	0
13	nBuCl	0.40	0	0

Three important points can be noted. In the ground state, first the solvent induced spectral shift is clearly governed by the  $\beta$ parameter for all compounds. We can observe that increasing solvent basicity induces a bathochromism in the CT band (b <0). Consecutive to the lability enhancement of the hydroxylic hydrogen, the presence of a negative partial charge on the oxygen atom should promote mesomeric interactions and lead to a more planar geometry. The values of the twist angles calculated for the corresponding zwitterion forms<sup>47</sup> confirms such a planarization tendency. The absorption CT band is consequently shifted to the low-energy side of the spectrum. Second, in the excited state, an important contribution for the fluorescence band shift stems from solute-solvent polarity interactions. The stabilizing effect (p < 0) increases with steric hindrance around the phenol-pyridinium bond. We have here another confirmation that enhanced twist angle provides a charge-transfer enhancement at excited states. Third, the Hbond-accepting property of the solvent contributes to a strong destabilization of the excited state (b > 0). This effect is very pronounced for highly twisted compound. For instance, the contribution of the solvent basicity accounts for 37% of the total spectral shift for PhPy1; this value rises to 52% for PhPy4. As previously observed for PhPy1,71 the energy level of the emitting excited states rises by increasing the solvent basicity. Therefore, we confirm and extend such an atypical effect to more twisted



TABLE 5: Kamlet-Taft Coefficients of Chromophores

Figure 7. Plots of the calculated maxima of fluorescence as function of the corresponding experimental maximum for various solvents.

compounds. Scheme 2 depicts the sequential steps leading to the deactivation of the excited biaryl derivatives. Because of a very efficient nonradiative deactivation pathway associated with the phenolate-like species generated from ESPT and with the assumption that this latter process constitutes the major relaxation channel from both LE and CSh states, this  $\beta$  dependence effect should be ascribed to a dramatic increase of the excited-state proton-transfer rate for highly twisted conformation (i.e.,  $k_{pt}^{LE} \ll k_{pt}^{CSh}$  in Scheme 2). Such a differential aspect can be explained by a better solvent stabilization of the excited twisted phenolate form (ESPT<sup>CSh</sup>) with respect to that of the more planar one (ESPT<sup>LE</sup>). It should be stressed that the fluorescence band hypsochromy upon increasing solvent basicity is an indirect effect of the differential deactivation of the excited twisted species.

Moreover, the evolution of the fluorescence quantum yields  $(\Phi_f)$  and fluorescence lifetimes in various solvent confirms that the radiationless process is strongly correlated to the basicity of the solvent (Table 3): for instance, in ethanol,  $\Phi_f$  exhibits very weak values below  $10^{-3}$  whereas in trifluoroethanol, a non-H-bond accepting solvent,  $\Phi_f$  is at least multiplied by a factor 30 for PhPy4 to a factor 140 for PhPy1.

3.3. Fluorescence Properties in Glassy Matrix (77 K). To suppress the radiationless processes that are linked with the intramolecular twisting relaxation, fluorescence measurements are performed in a rigid medium. Figure 8A shows the fluorescence spectra of biaryl derivatives in a glassy matrix of ethanol at 77 K and Table 6 gathers the corresponding spectroscopic data. Each spectrum can be divided into three parts. First, the high-energy side of the spectrum corresponds to the emission of the LE state. The band is clearly blue-shifted with respect to that observed at room temperature. The band intensity is strongly temperature dependent since its value is multiplied by a factor 100 for PhPy1 to a factor 500 for PhPy4. Figure 9 shows the corresponding LE fluorescence decays for each compound. The fluorescence lifetimes that initially exhibit short values below 200 ps at room temperature are strongly increased in the glassy matrix with sizable values ranging from 2.20 ns for PhPy1 to 4.70 ns for PhPy4. Therefore, we have clear evidence that the radiationless processes associated with the conformational change in the excited state are mainly suppressed in rigid medium.

Second, the middle part of the spectrum exhibits a distinctive band. According to the time gated measurements, such a

SCHEME 2: Mechanism of Stepwise Photoreaction with Radiative and Radiationless Deactivation of the Primary (LE) and Secondary (CSh) Rotamer



structured band is assigned to the phosphorescence emission (inset Figure 8A). For all derivatives, the phosphorescence lifetime ( $\tau_p$ ) is longer than 1 s (as collected in Table 6) and suggests a  $\pi\pi^*$  character for the emitting triplet state. The phosphorescence exhibits a vibronic structure whose associated wavenumber is in 1200–1300 cm<sup>-1</sup> range. Such vibrational



**Figure 8.** Emission spectra of biaryl derivatives in glassy matrix of (A) ethanol (77K) and (B)  $CH_2Cl_2/ACN$ ,  $4\nu/1\nu$  mixed solvents (dashed lines: deconvoluted phosphorescence spectra). Insets: normalized time gated phosphorescence spectra (delay: 5 ms).

wavenumbers correspond to the symmetric interaryl stretching modes.<sup>72</sup> Whereas the gradual increase of the twist angle  $\Theta_{AD}$  leads to a slight red shift of the fluorescence band, the phosphorescence one is clearly blue-shifted with a concomitant increase of its relative spectral contribution. Hence, the spin—orbit coupling is promoted by a perpendicular conformation. This was also observed for twisted biphenyls that exhibit higher  $k_{ISC}$  than planar ones.<sup>27,73</sup> Indeed, the theoretically spin-forbidden  $T_1 \rightarrow S_0$  transition is assumed to be strengthened through vibronic mixing and singlet-state mixing with polarization normal to the molecular plane.<sup>74</sup>

Finally, the red-energy side of the spectrum clearly shows a broad band. It should be stressed that this band is totally invariant to the dilution effect, which excludes the emission of aggregates. The excitation spectrum is in excellent agreement with that collected from the LE band and both excitation anisotropy spectra are also equivalent. Therefore, we have clear indications that the red emitting species stems from the LE state. We propose that this new band is ascribed to the radiative deactivation of a phenolate-like species produced by an excitedstate proton tranfer process from the LE state. The fluorescence of the conjugated phenolate base can be detected in a rigid medium, as displayed in Figure 10A. Such broad bands are also located in the same spectral region but are markedly blue-shifted with respect to that of their corresponding acid forms. This spectral difference should be assigned to a more planar geometry for the LE state of the phenolate derivatives. The mesomeric interactions are indeed more efficient for the zwitterion species. Moreover, the phenolate-like species generated by ESPT exhibit long fluorescence lifetimes ranging from 3.93 ns for PhPy1 to 6.93 ns for PhPhy4, as can be derived from the fluorescence decay curves depicted in Figure 9. These values are quite comparable with that obtained for the zwitterion species (see Table 6). Interestingly, we can note in Figure 8A that the increase of the twist angle  $\Theta_{AD}$  leads to a red shift of the ESPT<sup>LE</sup> band with a clear increase of the ESPT-to-LE quantum yield ratio (see also Figure S1, Supporting Information). As shown in Table 6, this ratio is multiplied by a factor of 5 from PhPy1 to PhPh4. In the glassy matrix, the photoinduced intramolecular twisting relaxation is mainly suppressed. Therefore, only the sequential steps inherent in the deactivation of the LE state are occurring here (left side of Scheme 2). With the assumption

TABLE 6: Photophysical Properties in a Glassy Matrix of Ethanol and Mixed Solvents of CH<sub>2</sub>Cl<sub>2</sub>/ACN at 77 K

	$S_1$				$\mathbf{S}_1^{\mathrm{Zwi}}$	$T_1$				
	$v_{\rm LE}~({\rm cm}^{-1})$	$v_{\rm ESPT}~({\rm cm}^{-1})$	$\tau_{\rm LE}~({\rm ns})$	$\tau_{\rm ESPT}~({\rm ns})$	$\Phi_{\mathrm{ESPT}}/\Phi_{\mathrm{LE}}{}^a$	$\overline{\tau^d}$ (ns)	$v_{\rm P}~({\rm cm}^{-1})$	$\tau_{\mathrm{P}}(\mathrm{s})$	$\nu_{00} \ (\text{cm}^{-1})$	$\Delta_{\text{S-T}} \; (\text{kJ mol}^{-1})$
					EtOH (77 K)					
PhPy1	25380	19575	2.20	3.54	0.20	3.20	20530	3.01	1250	58.1
PhPy2	24810	17730	3.16	4.85	0.28	5.60	21185	2.51	1300	43.4
PhPy3	24750	16920	4.56	$5.35^{\circ}$	0.43	6.30	$22450^{b}$	1.87	1200	27.6
PhPy4	24940	16640	4.70	6.25 <sup>c</sup>	0.92	7.10	$22780^{b}$	1.84	1270	25.9
				CH	H <sub>2</sub> Cl <sub>2</sub> /ACN (77	K)				
PhPy1	25730		3.13			4.00	20800	0.87	1310	59.0
PhPy2	25000		3.62			4.80	21400	1.65	1290	43.1
PhPy3	24250		4.95			6.80	22480	1.55	1220	21.2
PhPy4	24850		5.72			7.25	22750	1.45	1190	25.2

<sup>*a*</sup> Ratio calculated after subtraction of phosphorescence emission. <sup>*b*</sup> Fit of the spectral profile to four Gaussians functions. <sup>*c*</sup> Presence of a short time component ( $\tau < 0.2$  ns) that represents less than 5% of the decay. <sup>*d*</sup> Fluorescence lifetimes of the zwitterion species (Zwi).



Figure 9. Time fluorescence decays of the LE and ESPT states of each biaryl derivative in a glassy matrix of ethanol (77 K). Insets: residual graphs relative to monoexponential fits.

that the ratio of radiative rate constants relative to LE and ESPT<sup>LE</sup> states does not change significantly from PhPy1 to PhPhy4, the correlation observed between the increase of the twist angle  $\Theta_{AD}$  and the relative growth of the ESPT<sup>LE</sup> band can be assigned to the increase of  $k_{pt}^{LE}$ . In good accordance Kamlet–Taft analysis, we have shown that a strongly twisted conformation leads to the enhancement of the acidity of the excited state.

It is noteworthy that ESPT is strongly dependent on the H-bond-accepting property of the solvent. To illustrate such a pre-eminent factor, we have performed the same experiment in a glassy matrix of CH<sub>2</sub>Cl<sub>2</sub>/ACN (4v/1v) mixed solvents. The basicity of the medium should be strongly reduced due to the presence of a large amount of dichloromethane. At room temperature, the fluorescence bands of the biaryl compounds can be used to probe the  $\beta$  parameter of this binary solvent mixture. According to the Kamlet–Taft linear correlations that were previously derived for each chromophore, the  $\beta$  parameter was then estimated to a value of ca. 0.16. This value, which is

intermediate to that of acetonitrile and dichloromethane, confirms the low basicity of the medium as compared to ethanol, which exhibits a  $\beta$  of ca. 0.75. Figure 8B presents the emission spectra of the compounds in a glassy matrix of CH<sub>2</sub>Cl<sub>2</sub>/ACN. As previously observed for ethanol, the fluorescence bands undergo a shift to the high-energy region with a noticeable intensity enhancement with respect to the fluorescence emission at room temperature. For instance, the fluorescence intensity for PhPhy1 and PhPy4 is multiplied by a factor 10 and 19, respectively. However, these enhancement factors are considerably lower than that measured in ethanol, which indicates that the nonradiative deactivation processes associated with conformational change at the excited state (e.g., ESPT<sup>CSh</sup>) are strongly reduced in CH<sub>2</sub>Cl<sub>2</sub>/ACN. Moreover, on going from PhPy1 to PhPh4, the fluorescence undergoes a strong band broadening. This spectral effect is ascribed to the increasing contribution of the red emitting phosphorescence whose spectra are displayed in Figure 8B. The phosphorescence bands were extracted from the global emission spectra using a time gated method (see



Figure 10. Emission spectra of zwitterion forms of PhPy1 (squares), PhPy2 (circles), PhPy3 (triangle), and PhPy4 (diamond) in a glassy matrix of (A) ethanol and (B)  $CH_2Cl_2/ACN$ , 4v/1v (77 K).

Supporting Information). Finally, the emission from the phenolatelike species was not detected whatever the biaryl derivative. This contrasts with the sizable emission of the conjugated phenolate base observed in the low-energy region and displayed in Figure 10B. Such a result indicates that excited-state proton transfer does not occur in a glassy matrix of CH<sub>2</sub>Cl<sub>2</sub>/ACN. The suppression of ESPT even for highly twisted compounds that exhibit an enhanced excited-state acidity suggests that proton transfer to solvent is clearly dependent on the nature of the solvent and on its H-bond-accepting propensity more particularly. The mechanism of excited-state proton transfer is indeed the result of successive fast steps<sup>32,35,40</sup> such as both solvation of the excited species (R\*OH) and byproduct, hydrogen bond formation between R\*OH and a specific solvent molecule, proton dissociation, and diffusion. Such processes proceed through distinctive time regimes. For instance, the excited-state proton-transfer dynamics from 8-hydroxypyrene-1,3,6-trisulfonate (HPTS)<sup>36</sup> to water is composed of a first step of  $\sim 0.3$  ps corresponding to the solvation of HPTS in the excited state, a second step of 2.2 ps for the solute-solvent hydrogen bond formation (R\*OH····S), and a longer time process of 87 ps within the proton is dissociated and diffuses. In a glassy matrix, solvation processes are mainly suppressed, which should particularly impact the stabilization of the ESPT level,<sup>40</sup> whose energy is intimately related to the solvation of the proton and the phenolate-like species.<sup>30,43</sup> As a consequence, the energy gap between LE and ESPT levels should drastically decrease as well as the exothermic character of the proton-transfer

reaction. This latter effect is responsible for a strong decrease of the proton-transfer rate constant in a glassy matrix. According to the activation model formalized by Agmon and Levine,<sup>75,76</sup> the intrinsic free-energy barrier for proton transfer ( $G_a$ ) is modified by the total free-energy change ( $\Delta G$ ) so that the rate of proton transfer ( $k_{pt}^{LE}$ ) may be correlated to an Arrhenius plot:

$$k_{\rm pt}^{\rm LE} = k_{\rm pt}^{\circ \rm LE} \exp\left(-\frac{G_{\rm a}}{RT}\right) \tag{8}$$

with

$$G_{\rm a} = \Delta G - G_{\rm a}^{\ \#} \tag{9}$$

 $k_{pt}^{\circ LE}$  and  $G_a^{\#}$ , which depend on the nature of the solvent, denote the intrinsic proton-transfer rate and an intrinsic barrier, respectively. Hence, the role of specific solute-solvent interaction is all the more decisive in a glassy matrix since it constitutes the ultimate driving force for the promotion of the breaking or formation of hydrogen bonds that should contribute to a decrease of the activation barrier. In a glassy matrix of CH<sub>2</sub>Cl<sub>2</sub>/ACN, due to the weak basicity of the medium that does not allow any relevant specific solute-solvent interaction, it is clear that the rate of proton transfer is too weak to observe any emission from the phenolate-like species. However, in glassy ethanol, solvent molecules in close contact with the excited chromophore (R\*OH) should mediate the proton-transfer reaction by the formation a solvent-ion pair R\*OH····S intermediate that promotes the proton dissociation. This mediating effect, which mainly stems from the H-bond-accepting property of ethanol, should lower the activation barrier for proton transfer and lead to the emission of the phenolate-like species.

## 4. Conclusion

The photophysical properties of a donor-acceptor biaryl family that incorporates a phenol and a pyridinium moiety into gradually twisted conformations have been investigated. In the ground state, the increase of the twist angle  $\Theta_{AD}$  leads to a progressive blue shift of the absorption CT band with a concomitant decrease of its intensity. Such an effect is well addressed within the framework of the Mulliken-Murrel. model which indicates that this approach is applicable in charge-shift process. In the excited state, a rapid charge transfer occurs within the LE state to generate the corresponding CSh state with a highly twisted geometry. The fluorescence emission and emissivity of biaryl compounds are strongly solvent dependent. The correlation of the solvent induced spectral shift with Kamlet-Taft parameters first confirms the role of the nonspecific dipole-dipole interaction but also indicates a strong  $\beta$  dependence. The  $\beta$ contribution is increasing with twist angle  $\Theta_{AD}$  and leads to an unusual destabilization of the excited emitting state. This effect was indirectly ascribed to a differential nonradiative deactivation of LE and CSh states. An excited-state proton-transfer process is proposed as the major radiationless pathway of both excited states, which leads to a nonemissive phenolate-like form in liquid medium. In a rigid glassy matrix, despite the absence of the intramolecular twisting relaxation, the fluorescence of the phenolate species is detected and confirms the ESPT from the LE state. The relative increase of the phenolate band with twist angle  $\Theta_{AD}$  suggests that the enhancement of the excited states acidity can be triggered by intramolecular twisting change.

**Supporting Information Available:** Fluorescence spectra. This material is available free of charge via the Internet at http:// pubs.acs.org.

#### **References and Notes**

(1) Gust, D.; Moore, T. A.; Moore, A. L. Acc. Chem. Res. 1993, 26, 198–205.

(2) Desvergne, J.-P.; Czarnik, A. W. *Chemosensors of Ion and Molecule Recognition*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; Vol. 492.

(3) Malval, J.-P.; Suzuki, S.; Morlet-Savary, F.; Allonas, X.; Fouassier, J.-P.; Takahara, S.; Yamaoka, T. J. Phys. Chem. A **2008**, *112*, 3879–3885.

(4) Malval, J.-P.; Morlet-Savary, F.; Allonas, X.; Foussier, J.-P.; Suzuki, S.; Takahara, S.; Yamaoka, T. *Chem. Phys. Lett.* **2007**, *443*, 323–

327. (5) Lehn, J.-M. Angew. Chem., Int. Ed. Engl. 1988, 27, 89.

(6) Marcus, R. A. J. Phys. Chem. **1989**, 93, 3078.

(7) Hirsch, T.; Port, H.; Wolf, H. C.; Miehlich, B.; Effenberger, F. J. Phys. Chem. B 1997, 101, 4525–4535.

(8) Park, J. W.; Lee, B. A.; Lee, S. Y. J. Phys. Chem. B 1998, 102, 8209-8215.

(9) Le, T. P.; Rogers, J. E.; Kelly, L. A. J. Phys. Chem. A 2000, 104, 6778–6785.

(10) Jin, M.; Malval, J.-P.; Morlet-Savary, F.; Chaumeil, H.; Defoin, A.; Batat, P.; Jonusauskas, G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2622–2630.

(11) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. Chem. Rev. 2003, 103, 3899-4032.

(12) Malval, J. P.; Morand, J. P.; Lapouyade, R.; Rettig, W.; Jonusauskas, G.; Oberlé, J.; Trieflinger, C.; Daub, J. *Photochem. Photobiol. Sci.* 2004,

3, 939–948. (12) Crehowski Z. D. Botkiowicz, K. Siemierszyk, A. Cowley, D. L.

(13) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

(14) Rettig, W. Angew. Chem., Int. Ed. Engl. 1986, 25, 971.

(15) Rettig, W.; Chandross, E. A. J. Am. Chem. Soc. 1985, 107, 5617.

(16) Leinhos, U.; Kühnle, W.; Zachariasse, K. A. J. Phys. Chem. 1991, 95, 2013.

(17) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; Leinhos, U.; Kühnle, W.; Zachariasse, K. A. J. Phys. Chem. **1992**, *96*, 10809.

(18) Sobolewski, A. L.; Domcke, W. Chem. Phys. Lett. 1996, 250, 428.
(19) Waluk, J.; Herbich, J. J. Chem. Phys. 1994, 188, 247.

(20) Haar, T. V.; Hebecker, A.; Il'ichev, J.; Jiang, Y.-B.; Kühnle, W.;

Zachariasse, K. A. Recl. Trav. Chim. Pays-Bas 1995, 114, 430.

(21) Maus, M.; Rettig, W.; Bonafoux, D.; Lapouyade, R. J. Phys. Chem. A **1999**, 103, 3388–3401.

(22) Maus, M.; Rettig, W. J. Phys. Chem. A 2002, 106, 2104-2111.

(23) Rettig, W.; Kharlanov, V.; Effenberger, F.; Steybe, F. Chem. Phys. Lett. 2005, 404, 272–278.

(24) Kharlanov, V. A.; Rettig, W.; Knyazhansky, M. I.; Makarova, N. J. Photochem. Photobiol. A: Chem 1997, 103, 45–50.

(25) Kharlanov, V. A.; Knyazhansky, M. I.; Bicherov, A. V.; Rettig, W. J. Photochem. Photobiol. A: Chem **2000**, *131*, 17–21.

(26) Rettig, W.; Kharlanov, V.; Maus, M. Chem. Phys. Lett. 2000, 318, 173-180.

(27) Kharlanov, V.; Rettig, W. Chem. Phys. 2007, 332, 17-26.

(28) Solntsev, K. M.; Huppert, D.; Agmon, N.; Tolbert, L. M. J. Phys. Chem. A 2000, 104, 4658–4669.

(29) Solntsev, K. M.; Huppert, D.; Agmon, N. J. Phys. Chem. A 1999, 103, 6984–6997.

(30) Solntsev, K. M.; Huppert, D.; Agmon, N. J. Phys. Chem. A 1998, 102, 9599–9606.

(31) Solntsev, K. M.; Huppert, D.; Tolbert, L. M.; Agmon, N. J. Am. Chem. Soc. **1998**, 120, 7981–7982.

(32) Huppert, D.; Tolbert, L. M.; Linares-Samaniego, S. J. Phys. Chem. A **1997**, 101, 4602–4605.

(33) Clower, C.; Solntsev, K. M.; Kowalik, J.; Tolbert, L. M.; Huppert, D. J. Phys. Chem. A **2002**, 106, 3114–3122.

(34) Tran-Thi, T.-H.; Gustavsson, T.; Prayer, C.; Pommeret, S.; Hynes, J. T. *Chem. Phys. Lett.* **2000**, *329*, 421–430.

(35) Genosar, L.; Cohen, B.; Huppert, D. J. Phys. Chem. A. 2000, 104, 6689–6698.

(36) Hynes, J. T.; Tran-Thi, T.-H.; Granucci, G. J. Photochem. Photobiol. A: Chem 2002, 154, 3–11.

(37) Tran-Thi, T.-H.; Prayer, C.; Millié, P.; Uznanski, P.; Hynes, J. T. J. Phys. Chem. A 2002, 106, 2244–2255.

(38) Solntsev, K. M.; Clower, C. E.; Tolbert, L. M.; Huppert, D. J. Am. Chem. Soc. 2005, 127, 8534–8544.

(39) Poizat, O.; Bardez, E.; Buntinx, G.; Alain, V. J. Phys. Chem. A 2004, 108, 1873-1880.

(40) Tolbert, L. M.; Solntsev, K. M. Acc. Chem. Res. 2002, 35, 19–27.
(41) Agmon, N.; Rettig, W.; Roth, C. J. Am. Chem. Soc. 2002, 124, 1089–1096.

(42) Silverman, L. N.; Spry, D. B.; Boxer, S. G.; Fayer, M. D. J. Phys. Chem. A 2008, 112, 10244–10249.

(43) Granucci, G.; Hynes, J. T.; Millié, P.; Tran-Thi, T.-H. J. Am. Chem. Soc. 2000, 122, 12243–12253.

(44) Szczepanik, B.; Obara, R.; Rothe, A.; Weigel, W.; Rettig, W.; Stachera, M.; Rotkiewicz, K. Pol. J. Chem. 2008, 82, 807–829.

(45) Diemer, V.; Chaumeil, H.; Defoin, A.; Fort, A.; Boeglin, A.; Carré, C. *Eur. J. Org. Chem.* **2006**, 272, 7–2738.

(46) Diemer, V.; Chaumeil, H.; Defoin, A.; Jacques, P.; Carré, C. *Tetrahedron Lett.* **2005**, *46*, 4737–4740.

(47) Boeglin, A.; Barsella, A.; Fort, A.; Mançois, F.; Rodriguez, V.; Diemer, V.; Chaumeil, H.; Defoin, A.; Jacques, P.; Carré, C. *Chem. Phys. Lett.* **2007**, *442*, 298–301.

(48) Meech, R.; Phillips, D. J. Photochem. **1983**, 23, 193–217.

(49) Prazeres, T. J. V.; Fedorov, A.; Barbosa, S. P.; Martinho, J. M. G.;

Berberan-Santos, M. N. J. Phys. Chem. A 2008, 112, 5034–5039.

(50) Connor, D. V.; Phillips, D. *Time correlated single photon counting*; Academic Press: London, 1984.

(51) Ven, M. V. D.; Ameloot, M.; Valeur, B.; Boens, N. J. Fluoresc. 2005, 15, 377–413.

(52) HYPERCHEM, v. 7.03; Hypercube, Inc.: Gainesville, FL, 2002.

(53) Ephardt, H.; Fromherz, P. J. Phys. Chem. 1991, 95, 6792-6797.

(54) Fromherz, P.; Heilemann, A. J. Phys. Chem. 1992, 96, 6864-6866.

(55) Maus, M.; Rettig, W. Chem. Phys. 1997, 218, 151-162.

(56) Mulliken, R. S. J. Am. Chem. Soc. 1952, 74, 811.

(57) Murrel, J. N. J. Am. Chem. Soc. 1959, 81, 5037–5043.

(58) Berlman, I. B.; Steingraber, O. J. J. Chem. Phys. 1965, 43, 2140.

(59) Berlman, I. B. J. Chem. Phys. 1970, 52, 5616.

(60) Herbich, J.; Kapturkiewicz, A. J. Am. Chem. Soc. 1998, 120, 1014–1029.

(61) Dogonadze, R. R.; Kutznetsov, A. M.; Marsagishvili, T. A. *Electrochim. Acta* 1980, 25, 1.

(62) Suzuki, H. Electronic Absorption Spectra and Geometry of Organic Molecules; Academic Press: New York, 1967.

(63) Parr, R. G. J. Chem. Phys. 1952, 20, 1499.

 (64) Röcker, C.; Heilemann, A.; Fromherz, P. J. Phys. Chem. 1996, 100.
 (65) Birks, J. B. Photophysics of Aromatic Molecules; Wiley-Interview of the Markov and American Sciences (1970)

science: New York, 1970.
(66) Benniston, A. C.; Harriman, A.; Li, P.; Rostron, J. P.; Ramesdonk,
H. J. V.; Groeneveld, M. M.; Zhang, H.; Verhoeven, J. W. J. Am. Chem.

Soc. 2005, 127, 16054. (67) Lippert, E. Z. Naturforsch. 1955, 10a, 541.

 (68) Mataga, N.; Kaifu, Y.; Koizumi, M. Bull. Chem. Soc. Jpn. 1955, 28, 690.

(69) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. J. Org. Chem. 1983, 48, 2877–2887.

(70) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. J. Phys. Chem. **1994**, 98, 5807–5816.

(71) Malval, J.-P.; Diemer, V.; Morlet-Savary, F.; Jacques, P.; Allonas,

X.; Chaumeil, H.; Defoin, A.; Carré, C. Chem. Phys. Lett. 2008, 455, 238-

241. (72) Momicchioli, F.; Bruni, M. C.; Baraldi, I. J. Phys. Chem. 1972,

76, 3983–3990.

(73) Fujii, T.; Suzuki, S.; Komatsu, S. Chem. Phys. Lett. 1978, 57, 175.
 (74) Catalán, J. Chem. Phys. 2005, 316, 253–259.

(75) Agmon, N.; Levine, R. D. Chem. Phys. Lett. 1977, 52, 197.

(76) Agmon, N.; Levine, R. D. Is. J. Chem. 1980, 19, 330.

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