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Optical Behavior of Substituted 4-(2′-Hydroxyphenyl)imidazoles

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S Supporting Information

ABSTRACT: A set of tetraarylimidazoles bearing a 2-hydroxyphenyl substituent at position 4, as well as their models lacking intramolecular hydrogen bonds, was efficiently synthesized. Structural investigations proved that the hydrogen bond strength for 4-(2′-hydroxyphenyl)imidazoles is weaker than that for analogous 2-(2′-hydroxyphenyl)imidazoles as estimated from dihedral angles and bond distances. Photophysical investigations revealed that these compounds have other properties than those observed for imidazoles bearing a 2-hydroxyphenyl substituent at position 2. They exhibit a negligible fluorescence quantum yield regardless of the solvent polarity. Additionally, dual fluorescence is observed in nonpolar solvents. Plausibly, although a hydrogen bond is present within their chemical structure in the solid state, it is not clear if excited-state intramolecular proton transfer occurs. The presence of OH groups triggers the radiationless deactivation channel if compared with model imidazole possessing a 2-methoxyphenyl group.

λ_{em} = 403 nm
Φ_{fl} = 1%

λ_{em} = 428 nm
Φ_{fl} = 49%

λ_{em} = 445 nm
Φ_{fl} = 32%
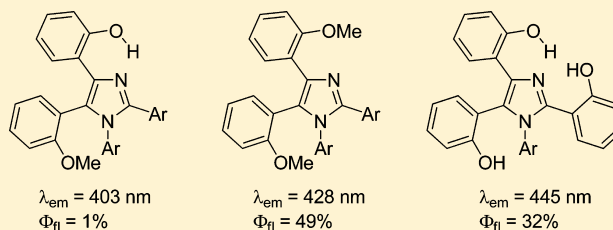
INTRODUCTION

The rising role of excited-state intramolecular proton transfer (ESIPT)[1] in modern optoelectronic applications is clearly visible, and can be exemplified by fluorescent probes,[2,3] molecular switches,[4] proton-coupled electron transfer,[5] and white-light-emitting diodes.[6] This research is often supported by advanced TD-DFT calculations, which allow one to gain in-depth insight into factors influencing ESIPT.[7,8] Among the popular ESIPT models, derivatives of 10-hydroxybenzo[*h*]-quinoline,[9−11] 2-(2′-hydroxyphenyl)imidazo[1,2-*a*]pyridine,[12−14] 2-(2′-hydroxyphenyl)benzoxazole,[15,16] 2-(2′-hydroxyphenyl)-benzimidazole,[17−19] 2-hydroxybenzaldehyde[20,21] and 3-hydroxyflavone predominate.[22,23] The derivatives of 2-(2′-hydroxyphenyl)-imidazoles[24−31] have recently attracted attention that derives from the combination of their excellent optical properties and modular synthesis. Surprisingly, among many derivatives studied, the compounds bearing 2-hydroxyphenyl substituents at position 4 were never investigated. The aim of this study was to synthesize exemplary compounds of this type, to investigate its optical properties and to compare them with those of 2-(2′-hydroxyphenyl)imidazoles.

EXPERIMENTAL SECTION

Synthesis. All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH$_2$Cl$_2$, hexanes) were distilled prior to use. Reported ^{1}H NMR and ^{13}C NMR spectra were collected using a 500 MHz spectrometer. Chemical shifts (δ, ppm) were determined with TMS as the internal reference; J values are given in Hz. The melting points of compounds were determined using a capillary type apparatus. The mass spectrum was obtained via electron impact MS (EI-MS).

Compounds **1**[32] and **10**[33] were prepared according to established protocols.

4,5-Bis(2′-hydroxyphenyl)-1-(4-methylphenyl)-2-(4-tri-fluoromethylphenyl)-imidazole (6). 4-Trifluoromethylbenzaldehyde (1.75 g, 1.0 mmol), 1,2-bis(2′-hydroxyphenyl)-1,2-ethanedione (2.43 g, 1.0 mmol), *p*-toluidine (1.61 g, 1.5 mmol), and ammonium acetate (3.85 g, 5.0 mmol) were added to a 150 mL three-necked flask. Glacial acetic acid (80 mL) was added under argon, and the resulting mixture was stirred at 110 °C for 18 h. After cooling, the solution was poured into an ice water mixture (500 mL). The white precipitate was filtered and washed with 1 L of water in small portions. The residue was dissolved in methanol (100 mL), concentrated under a vacuum, and finally dissolved in ethyl acetate (2 × 100 mL) and evaporated to yield 6.51 g of off-white solid. Crude product was crystallized from an EtOAc/hexanes 3:1 mixture. Yield 1.64 g (34%). mp 246.5−248.7 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 12.59 (bs, 1H), 7.54−7.48 (m, 4H), 7.30−7.26 (m, 1H), 7.13−7.06 (m, 3H), 7.02−6.90 (m, 6H), 6.86−6.81 (m, 1H), 6.60−6.55 (m, 1H), 5.39 (bs, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 159.6, 157.2, 146.79, 142.1, 141.1, 135.8, 135.1, 134.0, 133.2 (q, J = 32.3 Hz), 132.1, 131.7, 131.2, 130.1, 128.0, 127.9 (3 signals), 127.7, 123.6, 121.7, 120.1, 119.2, 118.9, 118.7, 23.9. MS (EI): 487.1 (40%), 486.1 (100%), 469.1 (16%), 396.1 (12%), 315.0 (12%), 262.0 (30%).

HRMS (EI): m/z calcd for $C_{29}H_{21}F_3N_2O_2$, 486.1555; found, 486.1553 $[M + H]^+$.

4,5-Bis(2′-hydroxyphenyl)-1-(p-tolyl)-2-(2′-hydroxyphenyl)-1H-imidazole (7). Prepared from 2-hydroxybenzaldehyde (0.62 g, 5.0 mmol) following a procedure described for compound **6**. Reaction time: 20 h. Yield: 1.02 g (47.0%). mp 221.0–224.9 °C. ^1H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.25–7.04 (m, 7H), 7.03–6.91 (m, 5H), 6.91–6.84 (m, 1H), 6.84–6.78 (m, 1H), 6.65–6.52 (m, 3H), 2.33 (s, 3H, OCH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 156.7 (C^{IV}), 155.6 (C^{IV}), 154.5 (C^{IV}), 144.5 (C^{IV}), 139.4 (C^{IV}), 135.7 (C^{IV}), 133.3 (C^{IV}), 132.6 (CH), 131.3 (CH), 131.0 (CH), 130.2 (CH), 129.5 (CH), 128.2 (CH), 127.6 (CH), 126.8 (CH), 125.3 (C^{IV}), 120.9 (CH), 119.7 (CH), 119.0 (CH), 117.5 (CH), 117.2 (CH), 116.5 (C^{IV}), 116.2 (CH), 115.9 (C^{IV}), 113.0 (C^{IV}), 21.3 (CH$_3$). MS (EI): 435.0 (36%), 434.0 (100%), 433.0 (48%), 417.0 (11%), 327.0 (10%), 209.9 (15%). HRMS (EI): m/z calcd for $C_{28}H_{22}N_2O_3$, 434.1606; found, 434.1630 $[M]^{•+}$.

4,5-Bis(2′-hydroxyphenyl)-1-(p-tolyl)-2-(p-methoxyphenyl)-1H-imidazole (8). Prepared from (4-methoxybenzaldehyde (0.68 g, 5.0 mmol) following the procedure described for compound **6**. Reaction time: 20 h. Yield: 1.04 g (47.0%). mp 233.3–235.3 °C. ^1H NMR (500 MHz, CDCl$_3$): δ (ppm) 7,32 (d, J = 8.8 Hz, 2H), 7.27–7.21 (m, 1H), 7.08–7.02 (m, 3H), 7.01–6.93 (m, 6H), 6.82–6.75 (m, 3H), 6.57–6.52 (m, 1H), 3.78 (s, 3H, OCH$_3$), 2.29 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 160.3 (C^{IV}), 156.8 (C^{IV}), 154.9 (C^{IV}), 145.5 (C^{IV}), 139.0 (C^{IV}), 133.3 (C^{IV}), 132.4 (CH), 131.2 (CH), 130.1 (CH), 129.9 (CH), 129.8 (CH), 128.9 (CH), 127.7 (C^{IV}), 127.6 (CH), 125.6 (CH), 120.7 (C^{IV}), 120.6 (CH), 119.1 (CH), 117.5 (CH), 116.2 (C^{IV}), 116.1 (CH), 113.9 (CH), 113.8 (C^{IV}), 55.3 (OCH$_3$), 21.2 (CH$_3$). MS (EI): 449.0 (34%), 448.0 (100%), 447.0 (40%), 431.0 (7%), 358.0 (9%), 314.9 (6%). HRMS (EI): m/z calcd for $C_{29}H_{24}N_2O_3$, 448.1785; found, 448.1787 $[M]^{•+}$.

4-(2′-Hydroxyphenyl)-5-(2′-methoxyphenyl)-1-(p-tolyl)-2-(p-trifluoromethylphenyl)-1H-imidazole (9). To a 100 mL three-necked flask equipped with a magnetic stirrer, cooler, and thermometer were added 4,5-bis(2′-hydroxyphenyl)-1-(p-tolyl)-2-(p-trifluoromethylphenyl)-1H-imidazole (195.0 mg, 0.4 mmol, 4.0 equiv), potassium carbonate (230.0 mg, 4.0 mmol, 10.0 equiv), and acetone (20 mL). Under argon, iodomethane (230.0 mg, 1.6 mmol, 1.5 equiv) was added and the resulting mixture was stirred at IT = 50 °C (oil bath 55 °C) for 18 h. After cooling, the solution was filtered and washed with acetone. Filtrate and washes were combined and evaporated under a vacuum. The residue was suspended in water (50 mL), and product was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were washed with water and brine, dried over Na$_2$SO$_4$, and evaporated. Crude product was crystallized from an EtOAc/hexanes mixture. The white precipitated powder washed with an EtOAc/hexanes 3:1 mixture was dried under a vacuum (18 h, oil pump, RT). Yield: 100.0 mg (50.0%). mp 113.6–114.8 °C. ^1H NMR (500 MHz, CDCl$_3$): δ (ppm) 12.68 (bs, 1H, OH), 7.51 (dd, J = 12.6, 8.7 Hz, 4H), 7.34 (dt, J = 8.7, 1.5 Hz, 1H), 7.22 (dd, J = 7.5, 1.5 Hz, 1H), 7.11–6.95 (m, 8H), 6.81 (d, J = 8.3 Hz, 1H), 6.54 (t, J = 7.8 Hz, 1H), 3.55 (s, 3H, OCH$_3$), 2.32 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 158.0 (C^{IV}), 156.9 (C^{IV}), 142.5 (C^{IV}), 138.9 (C^{IV}), 137.0 (C^{IV}), 133.7 (C^{IV}), 133.1 (CH), 132.6 (C^{IV}), 131.1 (CH), 130.2 (CF$_3$) (q, J = 32.3 Hz), 129.6 (CH), 128.5 (CH), 128.3 (CH), 128.1 (C^{IV}), 127.5 (CH), 125.9 (CH), 125.2 (C^{IV}), 125.1 (CH), 122.8 (C^{IV}), 120.9 (CH), 119.0 (CH), 118.6 (CH),

117.4 (CH), 117.1 (CH), 111.1 (C^{IV}), 55.2 (OCH$_3$), 21.2 (CH$_3$). MS (EI): 501.0 (34%), 500.1 (100%), 499.0 (11%), 469.0 (8%), 448.1 (12%), 261.9 (74%). HRMS (EI): m/z calcd for $C_{30}H_{23}F_3N_2O_2$, 500.1714; found, 500.1712 $[M]^{•+}$.

4,5-Bis(2′-methoxyphenyl)-1-(p-tolyl)-2-(p-trifluoromethylphenyl)-1H-imidazole (11). Product was prepared following the procedure described for compound **6**. Product was isolated by column chromatography on silica. Eluent mixture hexane ethyl acetate with gradient 9:1 → 7:3. Yield: 1.2 g (77%). mp 71.5–74.8 °C. ^1H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.65 (dd, J = 7.5, 1.7 Hz, 1H), 7.32 (dd, J = 36.7, 8.2 Hz, AA′BB′, 4H), 7.24–7.15 (m, 2H), 7.05–6.91 (m, 6H), 6.79–6.72 (m, 2H), 6.70–6.66 (m, 1H), 3.34 (s, 3H, OCH$_3$), 3.30 (s, 3H, OCH$_3$), 2.31 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 156.9 (C^{IV}), 156.3 (C^{IV}), 145.1 (C^{IV}), 137.9 (C^{IV}), 136.8 (C^{IV}), 135.0 (C^{IV}), 134.3 (C^{IV}), 132.0 (CH), 131.4 (CH), 130.2 (CH), 129.5 (CH), 129.5 (CF$_3$) (q, J = 32.3 Hz), 129.2 (CH), 129.1 (CH), 128.4 (CH), 127.4 (C^{IV}), 124.9 (CH), 124.8 (CH), 123.9 (C^{IV}), 120.8 (C^{IV}), 120.5 (CH), 120.2 (CH), 110.6 (CH), 110.3 (CH), 55.8 (OCH$_3$), 54.5 (OCH$_3$), 21.1 (CH$_3$). MS (EI): 515.0 (43%), 514.0 (100%), 512.9 (44%), 483.0 (64%), 407.0 (23%), 261.9 (82%). HRMS (EI): m/z calcd for $C_{31}H_{25}F_3N_2O_2$, 514.1863; found, 514.1860 $[M]^+$.
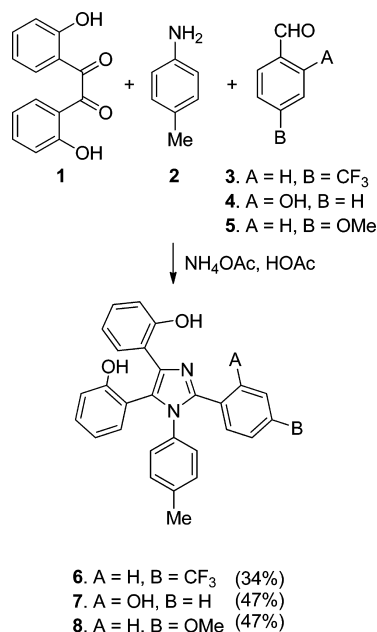
Optical Measurements. Electronic absorption spectra were collected on a UV−vis absorption spectrometer Lambda 35 (PerkinElmer, Rodgau, Germany). The spectra were corrected with solvent absorption spectra. Steady-state fluorescence emission spectra were collected on an FLS920-stm spectrometer (Edinburgh Instruments, Livingstone, United Kingdom). The spectra were corrected for the detector response. Fluorescence decays were also acquired on the FLS920-stm spectrometer using the time correlated single photon counting (TCSPC) technique with a sub-nanosecond pulsed LED (EPLED 320) as an excitation source. Fluorescence decay times were determined from the decays using the least-squares fitting method. The fitting was assumed to be correct when the goodness-of-fit value χ^2 was lower than 1.2. Fluorescence quantum yields were measured on a C9920-02G absolute QY measurement system from Hamamatsu (Hamamatsu Photonics Deutschland GmbH, Herrsching am Ammersee, Germany). All measurements were executed using 3 mL quartz cuvettes (Hellma GmbH, Jena, Germany) with a 1 cm light path. All measurements were executed for samples with OD below 0.15.

RESULTS AND DISCUSSION

The nature of Debus−Radziszewski imidazole synthesis[34] suggested that the use of 1,2-diketone, lacking D2 symmetry, should unequivocally result in a mixture containing two regioisomers (most probably inseparable). We also reasoned that the presence of the second 2-hydroxyphenyl substituent at position 5 should not influence the occurrence of ESIPT. Consequently, we set up reactions of 4-trifluoromethylbenzaldehyde (**3**) (or 4-methoxybenzaldehyde (**5**)) with 1,2-bis(2′-hydroxyphenyl)ethane-1,2-dione (**1**) and p-toluidine (**2**) under classical conditions. The resulting imidazoles **6** and **8** have been isolated in yields of 34 and 47%, respectively (Scheme 1).

The ability to reach clear conclusions about excited state processes in these compounds is only possible when their photophysical properties are compared to the corresponding models. Therefore, we designed additional tetrasubstituted imidazole **7** from salicylaldehyde (**5**) to obtain a derivative that possesses a 2-hydroxyphenyl group not only at positions 4 and 5 but also at a "classical" position 2 (Scheme 1). The model system for our

Scheme 1. Synthesis of Tetraaryl-Imidazoles 6–8

3. A = H, B = CF₃
4. A = OH, B = H
5. A = H, B = OMe

NH₄OAc, HOAc

6. A = H, B = CF₃   (34%)
7. A = OH, B = H   (47%)
8. A = H, B = OMe   (47%)

study was compound **11** possessing MeO groups instead of two OH groups. Initially, we attempted the synthesis of this derivative by methylation of compound **6** with excess of MeI under basic conditions (Scheme 2).

Scheme 2. Synthesis of Tetraaryl-Imidazole 9

6

MeI, K₂CO₃
acetone, 50%

9
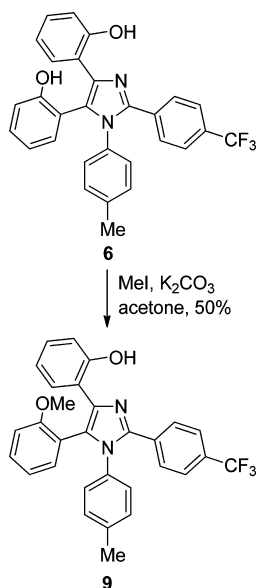
Under such conditions, only monomethylated compound **9** was isolated in 50% yield. Neither second possible regioisomer nor dimethoxy-derivative **11** was present in the reaction mixture. Apparently, the presence of a hydrogen bond differentiates the reactivity of hydroxyl groups, the same way as it is known for 2,4-dihydroxybenzaldehyde.[35] In light of this result, we changed our synthetic strategy. 1,2-Bis(2′-methoxyphenyl)-1,2-ethanedione (**10**) was prepared starting from 2-methoxybenzaldehyde in two steps according to a known procedure. The ketone **10** subjected to Debus−Radziszewski reaction swiftly afforded desired imidazole **11** in 77% yield (Scheme 3).
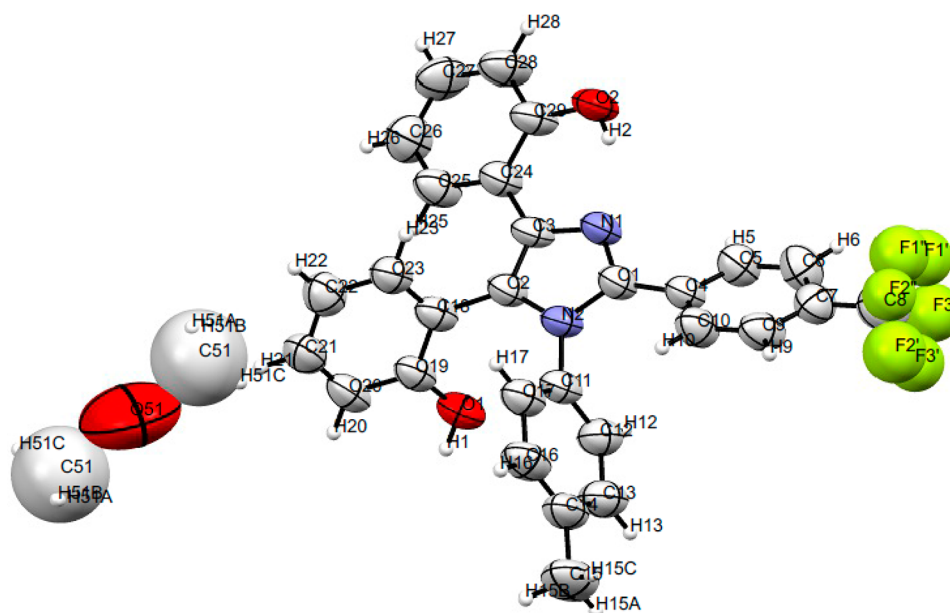
Scheme 3. Synthesis of Tetraaryl-Imidazole 11

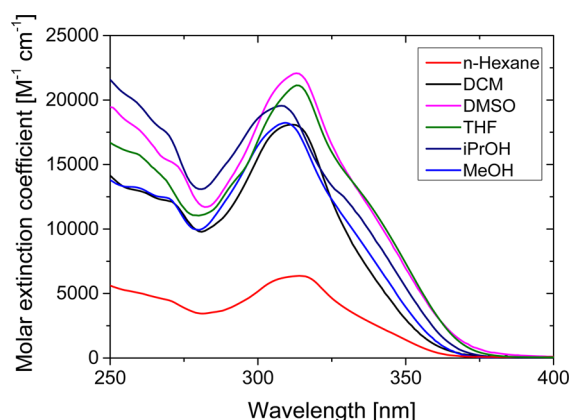10   2   3

NH₄OAc, HOAc, 77%

11
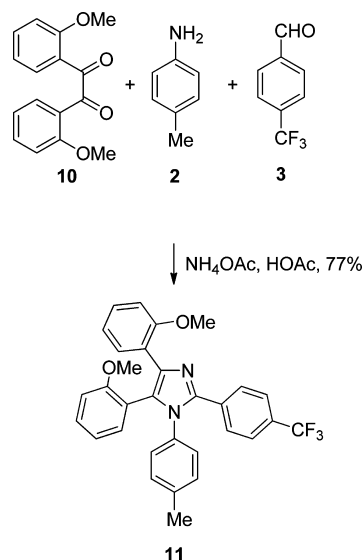
For compounds **6** and **9**, we could obtain X-ray quality crystals (Figures 1 and 2). In addition to serving as the final proof of identity (especially for imidazole **9**), these crystallographic structures allow us to study the presence of hydrogen bonds in the solid state (Figures 1 and 2). The dihedral angles between the aryl ring at position 4 and the imidazole plane are 10.6° (for compound **9**) and 15.7° (for compound **6**), respectively. It means that the conformation is less planar than in the case of 2-(2′-hydroxyphenyl)imidazoles described by Park and co-workers (dihedral angles = 2.2−2.7°).[36] A similar dihedral angle (4.3°) has been observed by Eseola et al. for an analogous imidazole derivative.[31] Noteworthy, for tetrasubstituted imidazoles lacking any substituents at the ortho positions of phenyl rings, the typical dihedral angles between phenyl rings are 15−56° (position 2) and 25−48° (position 4).[37,38] The length of the hydrogen bonds for known 2-(2′-hydroxyphenyl)-imidazoles is 1.54−1.81 Å,[39] while in our case they are equal to 1.85 Å (for **6**) and 2.02 Å (for **9**), respectively. Summing up the structural data, the hydrogen bond is considerably weaker in 4-(2′-hydroxyphenyl)imidazoles than in the case of 2-(2′-hydroxyphenyl)imidazoles and this factor will undoubtedly influence the excited state processes.

Absorption and fluorescence of the compounds **6−8**, **9**, and **11** have been determined in various solvents (Figures 1−6, Tables 1−6). According to expectations, the imidazoles **6−8**, **9**, and **11** absorb ultraviolet radiation with λ_{max} ~310−320 nm regardless of the solvent. For compounds possessing a 2-hydroxyphenyl group only at position 4 (i.e., **6**, **8**, and **9**), fluorescence is very weak and its maximum often strongly depends on solvent polarity (Tables 1, 4, and 5). In nonpolar, aprotic solvents, dual fluorescence is observed, and in the protic solvents, more bathochromically shifted fluorescence is present exclusively. When compared with 2-(2′-hydroxyphenyl)-imidazoles,[24−31] this fluorescence is significantly weaker with Φ_{fl} ~1%. We considered that a low emission yield could arise from fast nonradiative relaxation or form low-lying n states. To verify this hypothesis, we measured emission decays for **6** in various solvents. The primary excited state for this compound should be the singlet excited state of the enol-tautomer. One can expect to observe the fluorescence of the enol-tautomer after excitation at the red edge of the absorption band, since the

Figure 1. X-ray structure of compound **6**.

Figure 2. X-ray structure of compound **9**.

Stokes shift for the enol-tautomer should be relatively small. The decays were fitted simultaneously using a biexponential model, which gave decay times of 0.7−1.7 and 3.3−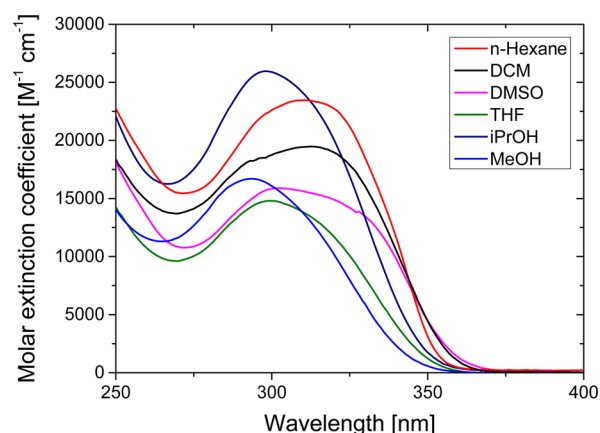6.9 ns, respectively. In MeOH, the fast component dominates the decay at 340 nm, which is expected to be the decay of the singlet excited state of enol-tautomer (Table 2). At 465 nm, the decay is almost monoexponential with a decay time of 7.5 ns. These results indicate that the UV-induced fluorescence is a direct emission from a locally excited state, while the origin of violet fluorescence is not clear.

Optical properties of imidazoles 7−9 and 11 add key information to this complexity. Analogous optical characteristics were detected for **8** and **9** (Tables 4 and 5). For imidazole **7**, possessing three 2-hydroxyphenyl groups at positions 2, 4, and 5, Φ_{fl} is significantly higher (0.32−0.60) and $\lambda_{(em)max}$

is different than those for compounds **6** and **8**; i.e., it is bathochromically shifted to ∼450 nm (Table 3), which corresponds well to previous data.[25−27] The Stokes shift is large, and it is clear that excited-state intramolecular proton transfer is a dominant process for compound **7**. It is noteworthy that imidazole **7** possesses high fluorescence quantum yields in solvents of all polarities. This is in striking contrast to 2-(2′-hydroxyphenylimidazoles) bearing phenyl groups at positions 4 and 5, which have much lower fluorescence in polar solvents.[26] On the other hand, fluorescence quantum yields of model compound **11** are high or very high (0.22−0.65) in the whole range of solvents (from hexanes to MeOH).

From the cross-comparison of these data, it is clear that the presence of the 2-hydroxyphenyl substituent at position 4 of imidazole causes strong perturbation of optical properties in

Figure 3. Electronic absorption spectra for compound **6** in various solvents.

Figure 5. Electronic absorption spectra for compound **11** in various solvents.

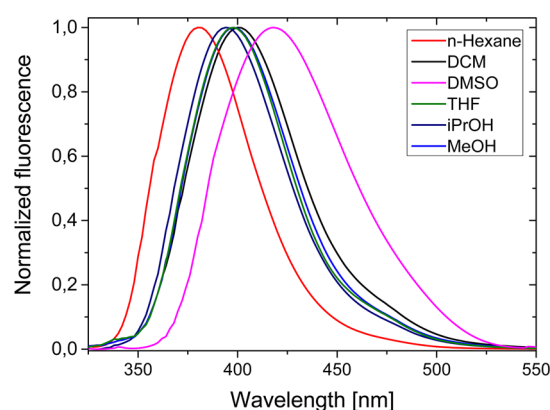**Figure 4.** Normalized fluorescence emission spectra (λ_{ex} = 295 nm) for compound **6** in various solvents.

Figure 6. Normalized fluorescence emission spectra (λ_{ex} = 295 nm) for compound **11** in various solvents.

this family of heterocycles. The weaker hydrogen bond between the phenolic OH and imino nitrogen atom is responsible for the different character of excited-state intramolecular proton transfer, if it occurs.

Closer examination of the structure of compound **6** reveals that it bears resemblance to 2-(2′-hydroxyphenyl)imidazo-[1,2-*a*]pyridines,[12−14,40−43] in terms of the position of the 2-hydroxyphenyl substituent vs two nitrogen atoms. As first observed by Douhal et al., it is impossible to draw a neutral keto tautomer for this class of compounds.[12] An analogous situation is in the case of 4-(2′-hydroxyphenyl)imidazoles (Scheme 4), and this is in contrast to the properties observed for 2-(2′-hydroxyphenyl)imidazoles, where a neutral keto structure can be drawn. The same authors also concluded that for the related 3-(2′-hydroxyphenyl)imidazo[1,5-*a*]pyridine the anomalous fluorescence is caused by significant changes in the geometry

of the emitting state following excitation and not to ESIPT. It seems that nontypical behavior of compounds **6**, **8**, and **9** makes it impossible to gain deeper insight into these phenomena. Unlike for 2-(2′-hydroxyphenyl)imidazoles, where in toluene and CH₂Cl₂ only ESIPT emission is observed, while in MeOH both keto and enol emissions are observed, for compound **6** in nonpolar solvents, only high energy emission under UV irradiation is observed.

In conclusion, we demonstrated that the presence of a 2-hydroxyphenyl substituent at position 4 of the imidazole ring triggers a completely different set of optical properties than in the case of 2-(2′-hydroxyphenyl)imidazoles. The new compounds possess a very low fluorescence quantum yield and dual emission in nonpolar solvents. The Stokes shifts are smaller than those for analogues possessing methoxy groups instead of hydroxyl groups. Fluorescence maxima are strongly

Table 1. Absorption and Emission of Compound 6 in Various Solvents

	solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	$\lambda_{em}{}^a$ (nm)	$\lambda_{em}{}^b$ (nm)	Φ_{fl}	$\Delta\nu$ (cm^{-1})	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	k_f (1/s) × 10^6	k_{nr} (1/s) × 10^8
nonpolar	*n*-hexane	314	6500	348, 382	380	0.005	3100, 5600	64	0.7	36	6.9	1.7	3.3
	DCM	311	18 000	362, 384	394	0.005	4500, 6100	57	1.3	43	3.3	2.3	4.6
polar aprotic	THF	314	21 000	362, 392	394	0.013	4200, 6300	53	1.7	47	4.5	4.3	3.3
	DMSO	313	22 000	426	420	0.011	8500	71	1.6	29	4.0	4.8	4.3
polar protic	iPrOH	309	19 500	409	403	0.007	7900	61	0.8	39	3.4	3.9	5.5
	MeOH	309	18 000	352, 409	385, 403	0.007	3900, 7900	89	1.0	11	5.7	4.6	6.5

$^a\lambda_{ex}$ = 295 nm. $^b\lambda_{ex}$ = 340 nm.

Table 2. Fluorescence Decay Times Determined for 6 Excited at 295 nm in MeOH[a]

λ_{em}*	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
340	1.21	69	1.03	31
365	0.88	76	1.91	24
405	0.85	80	3.40	20
440	0.70	89	4.89	11
465	0.70	95	7.53	5

[a]Fluorescence was collected at different emission wavelengths.

hypsochromically shifted versus the above-mentioned ESIPT-incapable analogues (~50 nm). Two decay times were determined for 4,5-bis(2′-hydroxyphenyl)-1-(4-methylphenyl)-2-(4-trifluoromethylphenyl)-imidazole regardless of the solvent. The very small Φ_{fl} observed for the studied compound regardless of the solvent suggests that significant nonradiative channels are activated in this case. Some data suggest that imidazoles bearing a 2-hydroxyphenyl substituent at position 2 do not display ESIPT behavior unless they also possess an additional 2-hydroxyphenyl group at position 2.

Scheme 4. Hypothetic Zwitterionic Structure after Proton Transfer for 4-(2′-Hydroxyphenyl)imidazoles
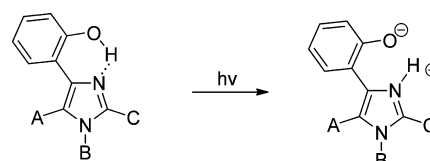
ASSOCIATED CONTENT

Ⓢ Supporting Information

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Table 3. Basic Photophysical Properties Determined for 7 in Various Solvents

	solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}	$\Delta\nu_1$ (cm^{-1})	τ (ns)[a]	k_f (1/s) × 10^8	k_{nr} (1/s) × 10^8
nonpolar	chloroform[b]	310	19 500	445	0.32	9700	1.2	2.6	5.5
	DCM	309	23 500	445	0.37	9800	1.4	2.7	4.6
polar aprotic	THF	307	20 500	445	0.55	10 000	3.1	1.8	1.5
	DMSO	306	19 000	445	0.31	10 200	3.7	0.8	1.8
polar protic	iPrOH	303	19 500	443	0.60	10 400	3.5	1.7	1.1
	MeOH	303	16 500	438	0.54	10 200	2.9	1.9	1.6

[a]λ_{ex} = 320 nm, λ_{ex} = 470 nm. [b]**7** is insoluble in *n*-hexane.

Table 4. Basic Photophysical Properties Determined for 8 in Various Solvents

	solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}	$\Delta\nu_1$ (cm^{-1})	τ_1[a] (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	k_f (1/s) × 10^6	k_{nr} (1/s) × 10^8
nonpolar	CHCl$_3$[b]	304	21 000	410	0.01	8500	1.3	70	2.9	30	5.5	5.4
	DCM	304	25 000	347	0.04	4000	1.2	80	8	20	15.6	3.8
polar aprotic	THF	305	30 000	357	0.01	4700	1.7	63	3.9	37	4.0	3.9
	DMSO	308	38 500	389	0.01	6700	1.6	100			6.3	6.2

[a]λ_{ex} = 320 nm, λ_{em} = 390 nm. [b]**8** is insoluble in *n*-hexane.

Table 5. Basic Photophysical Properties Determined for 9 in Various Solvents

	solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}	$\Delta\nu_1$ (cm^{-1})	τ_1[a] (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	k_f (1/s) × 10^6	k_{nr} (1/s) × 10^8
nonpolar	CHCl$_3$	314	17 000	403	0.01	7000	0.6	85	3.0	15	1.1	1.0
	DCM	313	24 000	335	0.01	2100	1.3	65	8.5	35	2.6	2.5
polar aprotic	THF	313	21 000	397	0.01	6700	2.0	80	6.1	20	3.6	3.5
	DMSO	315	48 000	417	0.01	7800	2.2	100			4.5	4.4
polar protic	iPrOH	311	23 000	401	0.01	7200	1.8	100			5.5	5.4
	MeOH	309	40 000	404	0.01	7600	1.5	100			6.6	6.5

[a]λ_{ex} = 320 nm, λ_{em} = 370−415 nm dependent on solvent.

Table 6. Basic Photophysical Properties Determined for 11 in Various Solvents

	solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}	$\Delta\nu$ (cm^{-1})	τ_1[a] (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	k_f (1/s) × 10^8	k_{nr} (1/s) × 10^8
nonpolar	CHCl$_3$	285	12 700	434	0.49	12 000	1.7	35	5.8	65	1.2	1.3
	DCM	286	16 300	428	0.27	11 600	2.2	85	6.1	15	1.0	2.6
polar aprotic	THF[b]											
	DMSO	286	15 000	440	0.49	12 200	1.0	85	5.3	15	3.0	3.1
polar protic	iPrOH	285	15 800	434	0.65	12 000	4.3	100			1.5	0.8
	MeOH	284	11 000	447	0.60	12 800	4.4	100			1.4	0.9

[a]λ_{ex} = 320 nm, λ_{em} = 430−470 nm dependent on solvent. [b]No data available.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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