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Strongly Emitting Fluorophores Based on 1-Azaperylene Scaffold

Daniel T. Gryko,* Joanna Piechowska, and Michał Gałęzowski

Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, Poland

daniel@icho.edu.pl

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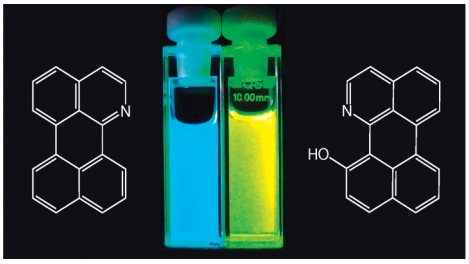

A novel blue-emitting polycyclic aromatic system was synthesized via anion-radical coupling. Its efficient direct hydroxylation led to a phenol possessing an intramolecular hydrogen-bond system. Since the energy gap difference between the enol and keto forms of this molecule is very small, characteristic of ESIPT chromophores, bathochromically shifted fluorescence was not observed.

Rigid aromatic systems, which contain heteroatoms in fused aromatic rings, are the subjects of considerable current research interest due to their fundamental optoelectronic properties and their potential applications such as light-emitting diodes, photovoltaic devices, and other organic optoelectronic devices.[1] During the past decades, attempts have been made to construct heterocyclic analogues of polycyclic aromatic hydrocarbons (PAHs) such as triphenylene, pyrene, and perylene.[2] Perylene is unique in the family of PAHs and has been extensively studied due to its excellent optical and electronic properties.[3] Incorporating heteroatoms into its skeleton is an intriguing target as this would induce a variety of intermolecular interactions, which is essential to achieve excellent device performance.[4,5]

In this context, as part of a broader investigation, we designed aza-analogue of perylene, namely 1-azaperylene (**2**). Neither 1-azaperylene nor its regioisomers have been synthesized before, and they are known only as products of coal tar extraction.[6] We focused our synthetic efforts on 1-azaperylene since the placement of the nitrogen atom in "the bay area" should allow such a molecule to be further functionalized using recently reported Pd-catalyzed reactions.[7] In particular, we anticipated that this compound would undergo acetoxylation[7a,b] at position 12 giving access to a derivative bearing an OH group.

The structure of such a molecule would in turn embrace a 10-hydroxybenzo[*h*]quinoline moiety, one of the best known chromophores, displaying excited-state intramolecular proton transfer (ESIPT). As 10-hydroxybenzo[*h*]quinoline[8] and other ESIPT chromophores[9] possess a large Stokes shift, many important applications (like laser dyes,[10] fluorescence recording,[11] ultraviolet stabilizers,[12] metal ion sensors,[13]

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probes for solvation dynamics[14] and biological environments,[15] and recently organic light-emitting devices[16]) have been found for them. Consequently, one important issue regarding the ESIPT system lies in the wide tunability of the chromophore absorption as well as proton transfer emission. We envisage that the chromophore expansion would influence the ESIPT phenomenon. We anticipated that 12-hydroxy-1-azaperylene would display ESIPT with bathochromically shifted absorption and emission compared to parent chromophore.

Our strategy toward the synthesis of 1-azaperylene was based on the assumption that the molecule containing both isoquinoline and naphthalene linked at positions 1 could be somehow oxidatively coupled at positions 8. Starting isoquinoline **1** was prepared using two independent methods.[17,18] The coupling reaction was initially attempted under typical Scholl conditions[19,20] ($FeCl_3$,CH_2Cl_2/$MeNO_2$, and $AlCl_3$/chlorobenzene), but both reactions led only to the recovery of starting material.

Subsequently, anion-radical coupling[21] was attempted using a method described by Müllen et al.[22] It is thought that electron transfer from metal to heterocycle leads to creation of anion radical species which is later oxidized and results in formation of new carbon−carbon bond. Stirring the isoquinoline **1** with potassium in anhyd 1,2-dimethoxyethane at room temperature followed by exposure to air resulted in the formation of desired product **2** in 12% (Scheme 1). Prolonging the exposure of the reaction mixture to air caused the formation of additional very polar tar material. Subsequently, 1,2-dimethoxyethane was replaced with toluene at 85 °C, leading to an appreciable increase in the yield. In this case, the reaction was quenched via addition of air-containing ethanol. Purification via chromatography afforded 1-azaperylene in 30% yield as yellow crystals. The same yield was achieved when reaction was performed on preparative scale.

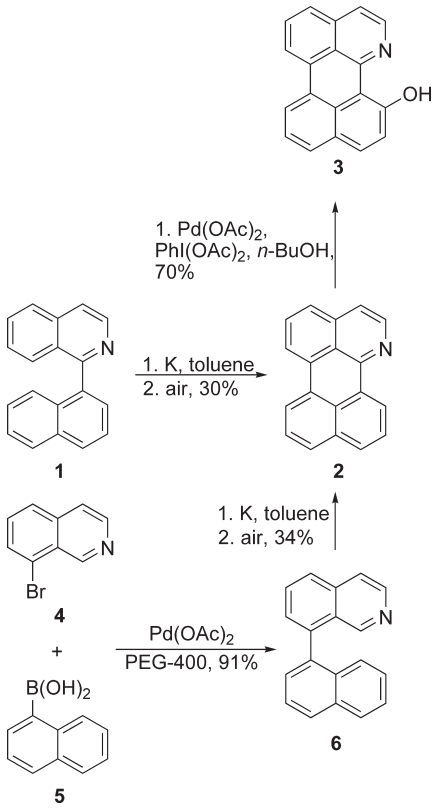
We envisioned that coupling could be more efficient for an analogous substrate **6**. Suzuki reaction of 8-bromoisoquinoline (**4**)[23] with naphthalene-1-boronic acid (**5**), performed under recently developed conditions,[24] led to required substrate **6** in 91% yield (Scheme 1). Subjecting this compound to anion-radical coupling conditions gave 1-azaperylene (**2**) in 34% yield.

The acetoxylation of 1-azaperylene was attempted via the Sanford reaction.[7a,b] Subjecting 1-azaperylene (**2**) to reported conditions ($PhI(OAc)_2$, $Pd(OAc)_2$, MeCN) resulted in the recovery of starting material. Extensive optimization studies identified alcohols as solvents of choice. This was rather surprising, since Sanford and co-workers reported that the reaction in alcohols led exclusively to the formation of ethers. In our hands, the reaction in ethanol gave 12-hydroxy-1-azaperylene (**3**) in 40% yield (Scheme 1). No corresponding ethoxyderivative was detected. The yield increased to 70% when the reaction was carried in *n*-butanol (60% on 1.25 mmol scale).

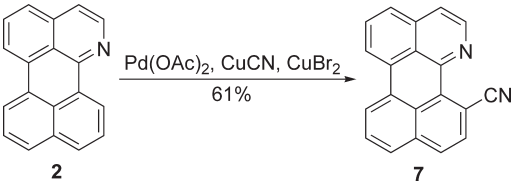
Compound **2** was also subjected to conditions for direct cyanation.[25] Reaction performed in the presence of CuCN led to 12-cyano-1-azaperylene (**7**) in 61% yield (Scheme 2).

The spectral characteristics of products **2**, **3**, and **7** were then examined (Figure 1, Table 1) and compared to those of the perylene and 10-hydroxybenzoquinoline. The most notable feature of the absorption spectrum of 1-azaperylene was its well visible vibrational structure (Figure 1). On the other hand, in analogy to anthracene/acridine absorption

SCHEME 1



SCHEME 2



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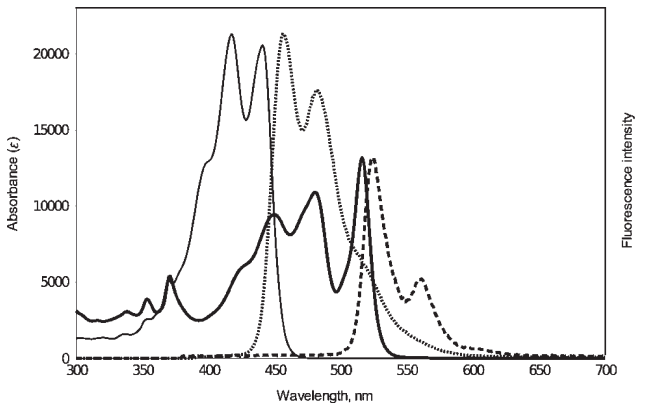

FIGURE 1. Absorption of **2** (solid line), absorption of **3** (bold line), emission of **2** (dotted line), and emission of **3** (dashed line) in CH_3CN.

TABLE 1. Spectroscopic Properties of Compounds 2, 3, and 7

compd	solvent	λ_{abs}/nm	λ_{em}/nm	Φ^a/%	Stokes shift (nm)
2	CH_3CN	417, 441	456, 482	nd	15
	cyclohexane	420, 444	448, 477	90	4
	EtOH	419, 442	463, 490	77	21
3	CH_3CN	481, 516	524, 561	nd	8
	cyclohexane	480, 516	519, 556	17	3
	EtOH	483, 516	523, 560	26	7
	$MeOH/H_2O^b$	482, 515	524, 559	36	9
7	CH_3CN	430, 458	478, 506	nd	20
	cyclohexane	423, 451	457, 487	84	6

[a]Determined using perylene or 9,10-bis(phenylethynyl)anthracene in cyclohexane as a standard. [b]$MeOH/H_2O$ ratio was 9:1.

spectra, the replacement of one carbon atom with nitrogen resulted in a very small bathochromic shift (λ_{max} (**2**) = 444 nm, λ_{max} (perylene) = 435 nm).

The fluorescence quantum yield of 1-azaperylene (**2**) was found to be high (Φ_{fl} (**2**) = 90% in cyclohexane and 77% in ethanol). Such a value could be attributed to a small possibility of internal rotations which often provide channels for nonradiative de-excitation. Absorption maximum of compound **7** was only slightly shifted versus that of parent compound **2** (Table 1). The Stokes shifts (nm) for compounds **2**, **3**, and **7** were small even in polar solvent (8−21 nm) (Table 1, Figure 1). The maximum emission wavelengths (λ_{em}) of **3** and **7** were moderately sensitive to the environment (15−21 nm longer in protic solvent). Compound **3** was a very intriguing case (Table 1). Due to the presence of auxochrome (OH), its absorption maximum was strongly bathochromically shifted by 75 nm in comparison to the 1-azaperylene (**2**). The characteristic feature of **3** was emission of greenish-yellow light (Φ_{fl} = 17−36%). Interestingly the fluorescence quantum yield of **3** is significantly higher in protic solvents than in cyclohexane. On the other hand, the maximum emission wavelength (λ_{em}) of **3** was only slightly sensitive to the environment (~ 5 nm longer in polar solvent, Table 1).

Surprisingly, no bathochromically shifted emission was detected, which is usually sign of ESIPT. In order to provide insight into this phenomenon, quantum molecular calculations were performed (time-dependent density functional theory (TDDFT, see the Supporting Information)). It revealed that in contrast to what was calculated[8e] and is

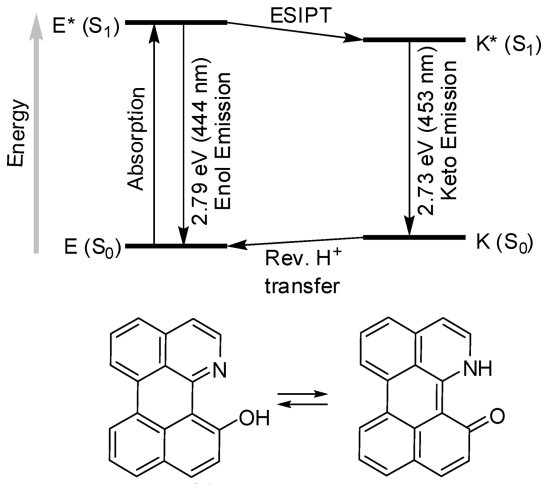

FIGURE 2. Diagram of the ESIPT process in the 12-hydroxy-1-azaperylene according to TD-DFT calculations (for more details, see the Supporting Information).

observed for 10-hydroxybenzo[*h*]quinoline, the energy difference between the S_1 and S_0 levels is only slightly smaller for keto-tautomer (K and K*) versus enol-tautomer (E and E*) (Figure 2). Moreover, the calculated energy difference in ground-state energies between keto and enol forms is very small (0.03 eV). The low-field resonance in the ^{13}C NMR spectrum (172.5 ppm versus 159 ppm for hydroxybenzoquinoline)[7a] seems to support these calculations. As a consequence, ESIPT cannot be clearly observed since ESIPT-derived fluorescence overlaps with the fluorescence of the enol-tautomer.

In conclusion, a new and efficient blue emitter, namely the aza-analogue of perylene, was synthesized from naphthalene and isoquinoline derivatives via an anion-radical coupling. 1-Azaperylene can be further functionalized at position 12 via Pd-catalyzed methods. Derivatives possessing hydroxy and cyano groups were efficiently prepared. We assume that excited-state intramolecular proton transfer occurs in 12-hydroxy-1-azaperylene, though due to the unfavorable energy levels the most pronounced effect is not clearly visible.

Experimental Section

1-Azaperylene (2). Method A: Compound **1** (4.0 g, 15.7 mmol) was dissolved in dry toluene (100 mL); subsequently, potassium (6.1 g, 157.0 mmol) was added under argon atmosphere. The reaction was stirred at 95 °C for 2 h, quenched with EtOH, filtered through Celite, and evaporated under reduced pressure. The residue was chromatographed (dry column vacuum chromatography,[26] Al_2O_3, hexanes/EtOAc, 95:5). The crystallization (CH_2Cl_2/petroleum ether) afforded pure product **2** as a yellow crystals (1196 mg, 30%): R_f = 0.32 (silica, CH_2Cl_2/acetone 99:1); mp = 250−251 °C; ^1H NMR (500 MHz, $CDCl_3$, δ) 7.43 (d, 1H, J = 5.6 Hz), 7.52 (t, 1H, J = 7.8 Hz), 7.59−7.66 (m, 3H), 7.79 (d, 1H, J = 8.1 Hz), 7.85 (d, 1H, J = 8.0 Hz), 8.21 (dd, 1H, J_1 = 1.0 Hz, J_2 = 7.1 Hz), 8.26 (d, 1H, J = 7.4 Hz), 8.51 (d, 1H, J = 5.6 Hz), 8.91 (d, 1H, J = 7.3 Hz); ^{13}C NMR (500 MHz, $CDCl_3$, δ) 119.6, 120.6, 121.6, 124.2, 124.3, 125.6, 126.4, 127.0, 129.0, 129.2, 130.5, 131.2, 132.8, 134.1, 137.3, 143.7, 152.1; EI-HR obsd 253.0889 [$M^{\bullet+}$], calcd exact mass 253.0892 ($C_{19}H_{11}N$); λ_{abs} (acetonitrile ε 10^{-3}) 441 (20.6), 417 (21.3), 370 (5.2), 337 (1.6),

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320 (1.4), 291 (1.6), 247 (27.8), 223 (21.9) nm; λ_{em} (cyclohexane) 448, 477 nm.

12-Hydroxy-1-azaperylene (3). 1-Azaperylene (**2**, 70 mg, 0.28 mmol), $PhI(OAc)_2$ (180 mg, 0.56 mmol), and $Pd(OAc)_2$ (7 mg, 0,032 mmol) were suspended in *n*-butanol (4.8 mL) in a heavy-wall pressure tube. The mixture was stirred at 150 °C for 25 h. Subsequently, the reaction mixture was chromatographed (Al_2O_3, hexanes/CH_2Cl_2, 3:1 then 2:1). The crystallization (MeOH) afforded the pure product **3** (52 mg, 70%). The reaction, performed on 1.25 mmol scale under the same conditions, afforded 204 mg (60%) of compound **3**: R_f = 0.34 (silica, CH_2Cl_2/acetone 9:1); mp = 260−265 °C; IR (KBr/cm^{-1}) 2923, 2853, 1744, 1629, 1590, 1562, 1285, 1211, 1125; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.12 (d, 1H, J = 6.4 Hz), 7.15 (d, 1H, J = 9.1 Hz), 7.42 (t, 1H, J = 7.7 Hz), 7.50 (d, 1H, J = 7.8 Hz), 7.73−7.77 (m, 3H), 7.80 (d, 1H, J = 9.2 Hz), 8.29 (d, 1H, J = 7.8 Hz), 8.38 (dd, 1H, J_1 = 0.8 Hz, J_2 = 7.8 Hz), 16.96 (br. s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$, δ) 115.6, 119.7, 122.8, 122.9, 123.4, 123.7, 124.7, 125.2, 126.7, 128.7, 130.1, 131.8, 132.7, 134.5, 135.8, 136,7, 152.3, 172.5; EI-HR obsd 269.0843 [$M^{\bullet+}$], calcd exact mass 269.0841 ($C_{19}H_{11}NO$); λ_{abs} (acetonitrile ε 10^{-3}) 516 (13.2), 481 (10.9), 450 (9.4), 371 (5.4), 353 (3.9), 316 (2.5), 283 (6.5); λ_{em} (cyclohexane) 519, 556 nm.

Acknowledgment. We acknowledge Polish Ministry of Science and Higher Education (contract T09A 50612) and thank Patricia Fleming for amending the manuscript.

Supporting Information Available: Experimental procedures and analytical data for compounds **2**, **6**, and **7**, ^{1}H NMR and ^{13}C NMR spectra for compounds **2**, **3**, **6**, and **7** as well as table of calculated energy levels. This material is available free of charge via the Internet at http://pubs.acs.org.