Communication

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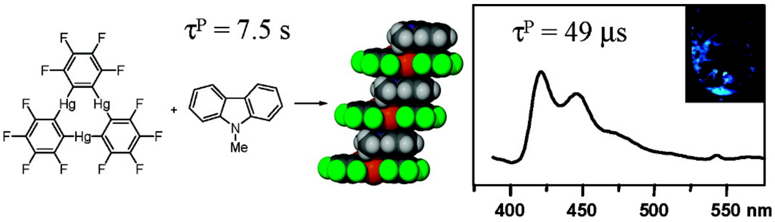

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Five-Order-of-Magnitude Reduction of the Triplet Lifetimes of *N*-Heterocycles by Complexation to a Trinuclear Mercury Complex

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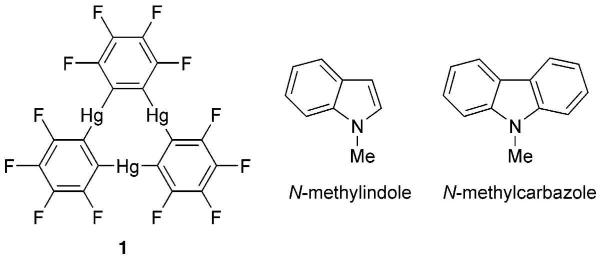
The heavy-atom induced phosphorescence of organic chromophores originates from spin−orbit coupling and is always accompanied by a reduction of the triplet excited-state lifetime. This phenomenon, which has been observed for a plethora of aromatic chromophores, can be triggered by both internal and external heavy atom effects.[1] In the latter case, a reduction of the triplet excited-state lifetime by 1 to 3 orders of magnitude has been observed.[1,2]

As shown by some of our recent work, trimeric perfluoro-*o*-phenylene mercury (**1,** Chart 1) "sticks" to the π-face of aromatic substrates.[3−5] In the case of pyrene, naphthalene, and biphenyl, this interaction leads to the formation of extended binary supramolecules in which **1** and the arene alternate.[6,7] In these supramolecules, each arene is surrounded by six mercury atoms that are positioned 3.3−3.6 Å from the arene molecular plane. As a result, the arene experiences a heavy-atom effect that is manifested by an intense $T_1 \rightarrow S_0$ monomer phosphorescence. This supramolecular approach allows for a systematic synthesis of bright phosphors whose emission colors can be coarse- and fine-tuned simply by varying the identity of the arene substrate.[6,7] Moreover, the triplet excited-state lifetimes fall in the millisecond range, which represents shortening by 3 to 4 orders of magnitude in comparison to those of the free arene. With the incorporation of such materials in OLEDs as an ultimate application,[8] we are currently exploring strategies that would afford lifetimes in the microsecond range.[9] Since chromophores with internal spin−orbit perturbation are typically more sensitive to external heavy-atom effects,[10] we have become interested in the photophysical properties of complexes involving **1** and *N*-methylcarbazole or *N*-methylindole (Chart 1) wherein the nitrogen atom acts as an internal spin−orbit coupling perturber.[1b,11]

Chart 1



1

N-methylindole

N-methylcarbazole

Incremental addition of **1** to a CH_2Cl_2 solution of the heterocycle results in a progressive quenching of the fluorescence of the heterocycle. The observed quenching most likely results from a mercury heavy-atom effect,[6,7] which depopulates the S_1 state of the heterocycle. Analysis of the fluorescence quenching data herein provides the first evidence for the complexation of aromatic substrates by **1** in solution. Thus, a Stern−Volmer analysis[12] yields a K_{SV} value of 2792 ± 68 M^{-1} for *N*-methylindole and 891 ± 40 M^{-1} for *N*-methylcarbazole (Figure 1). The magnitude of these constants suggests that the quenching observed is static rather than dynamic. This conclusion is reinforced by measurements of the fluorescence lifetimes, which remain constant during the titration experiment (Figure 1). Altogether, these observations clearly indicate the formation of *ground-state complexes in solution,* i.e., [**1**·*N*-methylindole] (**2**) and [**1**·*N*-methylcarbazole] (**3**) whose association constants are equal to the respective K_{SV}. The photoluminescence spectra of frozen CH_2Cl_2 solutions containing equimolar amounts of **1** and *N*-methylcarbazole or *N*-methylindole exhibit only the phosphorescence of the *N*-heterocycle (Figure 2) with emission energies that correspond to those reported for the respective T_1 states.[13,14] The observed phosphorescence results from substantial spin−orbit coupling provided by the mercury centers of **1** to the *N*-heterocycle, consistent with the existence of complexes **2** and **3** in solution. Measurements in frozen CH_2Cl_2 solutions indicate drastic lifetime shortening upon complexation ($\tau^P = 66 \pm 3$ μs for **2** and 176 ± 6 μs for **3** vs 2.1 s for *N*-methylindole and 5.1 s for *N*-methylcarbazole), certainly corroborating the above conclusion.

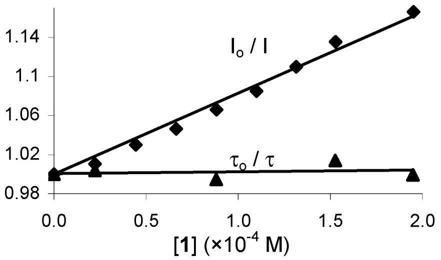


Figure 1. Stern-Volmer plots for the fluorescence quenching of *N*-methylcarbazole with **1**.

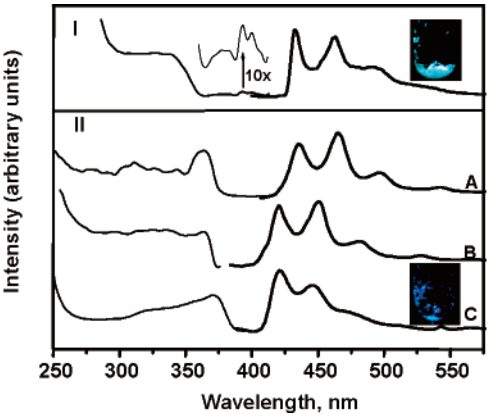


Figure 2. Photoluminescence excitation and emission spectra of crystals of **2** at 77 K (I) and of **3** (II) in CH_2Cl_2 frozen solution (A), crystals at 77 K (B), and crystals at room temperature (C).

While it is difficult to ascertain their structure in solution, the binary complexes precipitate from concentrated CH_2Cl_2 solutions

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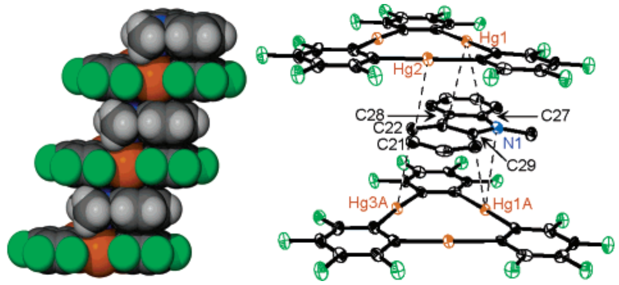

Figure 3. Space filling (left) and ORTEP view (50% ellipsoid, right) of a portion of a stack in the structure of **3.** Only one of the two crystallographically independent stacks is shown. Representative intermolecular distances (Å): Hg(1)−C(27) 3.37, Hg(1)−C(28) 3.27, Hg(1A)−C(29) 3.33, Hg(1A)−N(1) 3.39, Hg(2)−C(21) 3.29, Hg(3A)−C(22A) 3.38.

Table 1. Triplet Lifetimes for *N*-Heterocycles and Their Adducts with **1**

	EPA (s)	frozen CH_2Cl_2 (s)		frozen CH_2Cl_2 (μs)	solid 77 K (μs)	solid RT (μs)
N-methylindole	6.7	2.1	**2**	66	57	29
N-methylcarbazole	7.5	5.1	**3**	176	99	49

containing equimolar amounts of **1** and *N*-methylcarbazole or *N*-methylindole. As indicated by elemental analysis, the solid adducts have a 1:1 stoichiometry. While we have not been able to elucidate the solid-state structure of **2**, single crystals of **3** can be readily obtained. The crystal structure of this adduct reveals the formation of extended binary stacks with alternating molecules of **1** and *N*-methylcarbazole (Figure 3). As a result, the π-faces of the heterocycle are directly exposed to the trinuclear mercury core of adjacent molecules of **1**. Because of the presence of two independent molecules of [**1**·*N*-methylcarbazole] in the asymmetric unit, there are two crystallographically independent types of stacks which differ by the orientation of the *N*-methylcarbazole unit with respect to the trinuclear mercury core of **1**. In one of the two orientations, there is a short Hg−N distance of 3.39 Å, which is within the van der Waals radii of mercury (r_{vdw} = 1.7 Å)[15] and nitrogen (r_{vdw} = 1.5 Å).[16] In both stacks, there are short Hg−$C_{aromatic}$ contacts ranging from 3.26 to 3.44 Å, suggesting the presence of secondary Hg−π interactions.[6,7] The coexistence of two distinct orientations of the *N*-methylcarbazole unit suggests that these interactions are not directional but perhaps largely dispersive and/or electrostatic.

The solid-state photoluminescence spectra of crystalline **2** and **3** are almost identical to those observed for the corresponding frozen CH_2Cl_2 solutions (Figure 2). The intense emissions of the binary solids are attributed to monomer phosphorescence of *N*-methylindole and *N*-methylcarbazole, respectively.[13,14] In addition, the excitation spectrum of compound **2** features a series of bands that are distinctly red-shifted from the singlet absorption of the unperturbed heterocycle. These bands (Figure 2, I) most likely correspond to direct $S_0 \rightarrow T_1$ excitation. Nevertheless, the low intensity of these bands suggests that they play little role in the excitation route. To further assess the extent of the heavy atom effects induced by **1** in the solid state, we analyzed the kinetics of the radiative decay (Table 1). The phosphorescence lifetimes for solid **2** and **3** are below 100 μs at room temperature (RT) and 77 K (Table 1). The lifetimes at 77 K are shortened by 5 orders of magnitude, when compared to those of the free *N*-heterocycles in EPA glass[13,14] (Table 1). Such a startling reduction underscores the difference that exists in the spin−orbit perturbation provided by an innocent matrix such as EPA and the heavy-atom environment provided by the mercury atoms of **1** in the adducts. We also note that these lifetime reductions are more drastic than those obtained when comparing the triplet emissions of [**1**·biphenyl] or [**1**·naphthalene] to those of the respective free arenes.[6,7] Hence, the dramatic lifetime reduction observed for **2** and **3** most likely results from the synergy of the external mercury and internal nitrogen heavy atom effects. The combination of these effects is also manifested by the appearance of $S_0 \rightarrow T_1$ bands in the excitation spectrum of **2**. The $(\tau^P)^{-1}$ values measured at 77 K or RT represent the sum of the radiative (k_r) and nonradiative (k_{nr}) decay rate constants, which cannot be readily separated. Hence, we have carried out low-temperature lifetime measurements down to 4 K; extrapolation to 0 K yields $k_r = 1.53\ (0.01) \times 10^4\ s^{-1}$ for **2** and $2.92\ (0.02) \times 10^3\ s^{-1}$ for **3**. Assuming that the yield of intersystem crossing is unity, these measurements suggest that the RT phosphorescence quantum yield of **2** (44%) is greater than that of **3** (14%).

In conclusion, these studies indicate that adducts involving **1** and aromatic substrates exist in solution. Their presence is reflected by the intense phosphorescence observed in frozen solutions, and their formation can be readily quantified by fluorescence spectroscopy. More importantly, we describe a strategy that yields bright room-temperature phosphors whose excited-state lifetimes are below 100 μs, owing to heavy-atom effects. This strategy is based on the use of simple *N*-heterocyclic chromophores whose phosphorescence is induced and greatly accelerated by complexation to **1**. Current efforts are focused on the incorporation of these materials in light-emitting devices.

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Supporting Information Available: X-ray crystallographic data for **2** in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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