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Communication

Enhancement of the Phosphorescence of Organic Luminophores upon Interaction with a Mercury Trifunctional Lewis Acid

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The interaction of the trinuclear mercury(II) complex [(o-C_6F_4Hg)$_3$] (**1**) and pyrene leads to the formation of the 1:1 adduct **1·pyrene**. The crystal structure of this adduct reveals the existence of supramolecular stacks in which molecules of **1** and molecules of pyrene alternate along the infinite chains. Steady-state and time-resolved photoluminescence measurements indicate the occurrence of a heavy atom effect which results in red, green, and blue (RGB) phosphorescent emissions for **1·pyrene**, **1·naphthalene**, and **1·biphenyl**, respectively.

Polynuclear aromatic organic compounds usually display fluorescent emissions with no phosphorescence at room temperature. Special conditions such as cooling to 77 K in rigid glass solutions are usually required to observe phosphorescence. Owing to the spin-forbidden character of both the $S_1 \rightarrow T_1$ intersystem crossing and $T_1 \rightarrow S_0$ emission, these compounds usually exhibit long lifetimes and low quantum efficiencies.[1] Because of spin–orbit coupling, the presence of heavy atoms directly attached to the luminophore or positioned at its periphery can alter this situation.[2–4] While this phenomenon has been the object of extensive previous studies,[2–6] some of us recently reported[7,8] the facial complexation of aromatic hydrocarbons to trimeric perfluoro-*o*-phenylene mercury (**1**)[9] and showed that the emission spectra of the resulting adducts feature emission bands that correspond to the phosphorescence of the aromatic molecule.[8] With the incorporation of such materials in optoelectronic devices as a goal, it has become important to study (1) the generality of our approach by considering the assembly of **1** with alternative strongly luminescent luminophores and (2) the photophysical properties of the resulting supramolecules. In this vein, we now wish to communicate the synthesis and structure of **1·pyrene** (**2**) as well as photoluminescence steady-state and lifetime measurements of **2**, **1·naphthalene** (**3**), and **1·biphenyl** (**4**). This contribution elaborates on a series of earlier investigations concerning the use of trinuclear complexes for the generation of stacked supramolecules with unusual luminescence properties.[10,11]
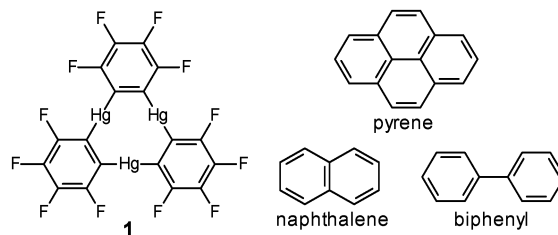
Phosphorescence enhancement for organic compounds in the solid state at ambient temperature is significant for organic light-emitting devices (OLEDs). While many organic emitters exhibit strong fluorescence with very high photoluminescence (PL) quantum yields (up to unity), an upper limit of only 25% theoretical internal electroluminescence (EL) quantum efficiency is usually associated with organic fluorophores because of spin statistics for the emitting singlet

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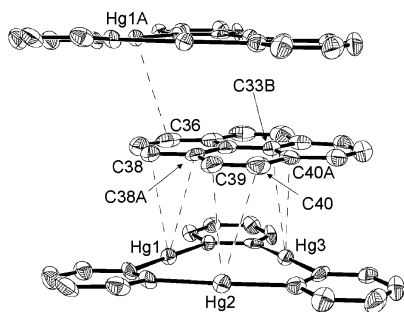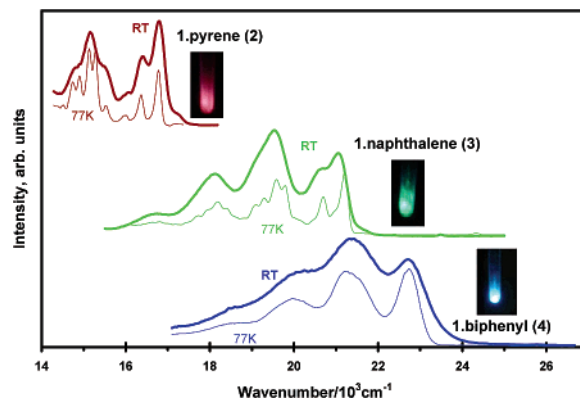
Figure 1. Molecular structure of **2**. Thermal ellipsoids are at 30%. Fluorine and hydrogen atoms are omitted for clarity. Significant contacts (Å): C(38)−Hg(1) 3.353(16), C(38A)−Hg(1) 3.460(14), C(39)−Hg(2) 3.487(16), C(40)−Hg(2) 3.553(17), C(33B)−Hg(3) 3.424(14), C(40A)−Hg(3) 3.408-(15), and C(36)−Hg(1A) 3.536(17).

Figure 2. Photoluminescence spectra for crystalline solids of **2**−**4**. Intensities of different spectra were adjusted arbitrarily for clarity. Photographs are shown for the emissions of crystalline solids at ambient temperature.

state (one singlet and a 3-fold degenerate triplet).[12] Due to the mixing of the singlet and triplet states in phosphorescent materials, the theoretical upper limit of the internal EL efficiency is 100%. Therefore, phosphorescent heavy metal complexes have been receiving increasing attention for OLED applications.[13] The luminophores described here are different in the sense that the presence of the metal acts merely to enhance the phosphorescence of the organic component with little disturbance of its emitting triplet state. Hence, one can systematically select the organic substrate with a control of the color and quantum yield of the phosphorescent emission sought.

While the synthesis of **1**·naphthalene (**3**) and **1**·biphenyl (**4**) has been described previously,[8] the mixing of **1** with pyrene in CS_2 or CH_2Cl_2 results in the spontaneous precipitation of **1**·pyrene (**2**) as a pale yellow solid. Single crystals of **2** can be obtained by slow diffusion of a CH_2Cl_2 solution of **1** into a CH_2Cl_2 solution of pyrene. The stoichiometry of **2** was confirmed by elemental analysis[14] and X-ray structural studies (vide infra).

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of **1** and one molecule of pyrene in the asymmetric unit (Figure 1).[15] The infinite stacks consist of alternating molecules of **1** and pyrene. Inspection of the crystal structure shows that molecules of **1** and pyrene are essentially parallel to one another. The sandwiched pyrene molecule engages in three dihapto interactions that involve

C(38)−C(38A) and Hg(1), C(39)−C(40) and Hg(2), and C(33B)−C(40A) and Hg(3). A short distance is also observed between C(36) and Hg(1A). The resulting $Hg\cdots C_{pyrene}$ distances, which range from 3.353 to 3.553 Å, are similar to those observed in the structures of **3** and **4**.[8]

PL spectra[16] are shown in Figure 2 for crystalline samples of **2**−**4**. The intense red emission of **2**, green emission of **3**, and blue emission of **4** are attributed to monomer phosphorescence of pyrene, naphthalene, and biphenyl, respectively. The emission energies of the phosphorescence bands shown in Figure 2 for **2**−**4** are very similar to the values reported in the literature for free pyrene, naphthalene, and biphenyl.[17−19] Excited-state lifetime measurements at (ambient temperature, 77 K) yielded $\tau = (568 \pm 8 \mu s, 423 \pm 8 \mu s)$, $(712 \pm 12 \mu s, 985 \pm 11 \mu s)$, and $(454 \pm 5 \mu s, 337 \pm 5 \mu s)$ for **2**, **3**, and **4**, respectively. These microsecond-level lifetimes clearly represent phosphorescence, in contrast to the monomer fluorescence bands exhibited by free pyrene, naphthalene, and biphenyl at much higher energies and with nanosecond-level lifetimes. The excited-state lifetimes measured in microseconds for **2**−**4** are much shorter than those reported for the monomer phosphorescence bands of the free arenes (0.7, 2.3, and 4.4 *seconds* for pyrene, naphthalene, and biphenyl in frozen glasses, respectively).[2b,20] The strong spin−orbit coupling effect due to the presence of mercury atoms[21] in **2**−**4** makes the phosphorescence transition from the triplet excited state of the organic component a more allowed transition, hence leading to shorter lifetimes than those exhibited by the pure organic compounds in which phosphorescence is strongly forbidden.

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(15) Crystal data for **2**: $C_{34}H_{10}F_{12}Hg_3$, M 1248.19, monoclinic, space group $P2_1/c$, $a = 21.908(4)$ Å, $b = 7.0456(14)$ Å, $c = 21.918(4)$ Å, $\beta = 117.61(3)°$, $V = 2998.0(10)$ Å^3, $Z = 4$, $\mu_{calc} = 2.765$ g cm^{-3}. Siemens APEX area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $T = 270$ K. Crystal size $0.64 \times 0.12 \times 0.04$ mm^3, ω-scan mode, measurement range $1.05° \leq \Theta \leq 23.74°$, 4335 unique reflections, $\mu = 15.426$ mm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using the SHELXTL/PC (version 6.1) package, 442 parameters, R1 = 0.0679, wR2 = 0.1481 (all data). Further crystallographic details can be found in the Supporting Information.

(16) Steady-state luminescence spectra were acquired with a PTI Quanta-Master Model QM-4 scanning spectrofluorometer equipped with a 75 W xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. Lifetime data were acquired using the 337.1 nm line of a N_2 laser and fluorescence and phosphorescence subsystem add-ons to the aforementioned instrument.

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The emission spectra of **2**−**4** exhibit well-defined vibrational features. These are essentially identical to those observed in the phosphorescence bands of the three arenes in various matrices at low temperature, which have been the object of detailed spectral analyses in the literature.[17−19] Excitation spectra of **2**−**4** (Supporting Information) show only weak signals due to direct $S_0 \rightarrow T_1$ arene absorption, suggesting that other photophysical processes lead to the observed $T_1 \rightarrow S_0$ phosphorescence.[22]

The results reported herein merit some comments. First of all, it appears that the π-complexation of polycyclic aromatic hydrocarbons by **1** is a general phenomenon that leads to the formation of binary stacks. Compounds **2**−**4**, which constitute prototypical examples of such supramolecular materials, display bright red, green, and blue (RGB) emissions in the solid state at ambient temperature. Because the energy of the emission is hardly affected by the presence of **1**, existing phosphorescence spectra of aromatic hydrocarbons can be used to predict and fine-tune the color of the emission of such binary materials.

The phosphorescence observed for **2**−**4** is due to monomers of the organic component. Strongly fluorescent polynuclear aromatic compounds like pyrene have very high PL efficiency in solution, but this efficiency drops in the solid state partially due to excimer formation, which is known to cause detrimental quenching to EL efficiencies.[23] For example, the blue structureless emission of solid pyrene is an excimer emission.[24] The structure of the 1:1 stacks of **2**−**4**

prohibits the formation of excimers. Therefore, our synthetic route represents a novel new strategy to inhibit excimer emissions in organic luminophores.

To conclude, the results presented herein show that the formation of binary supramolecular stacks by interaction of **1** with arenes is a general phenomenon. As a result of a mercury heavy-atom effect, the resulting materials display intense room temperature phosphorescence whose color can be adjusted by the choice of the arene. With such properties, these materials appear ideally suited for the development of electroluminsecent devices. In view of their incorporation into OLEDs, we are currently attempting to determine whether materials such as **2**−**4** exhibit electroluminescence.

Supporting Information Available: X-ray crystallographic data for **2** (CIF). Luminescence excitation spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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