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Sensitization of Naphthalene Monomer Phosphorescence in a Sandwich Adduct with an Electron-Poor Trinuclear Silver(I) Pyrazolate Complex

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Facial complexation of naphthalene to {[3,5-$(CF_3)_2$Pz]Ag}$_3$ (**Ag$_3$**) gives rise to a stacked binary adduct (**1**) that exhibits phosphorescence corresponding to T_1 monomer emission of naphthalene. Crystals and powders of **1** exhibit bright-green phosphorescence at room temperature with a 830 μs lifetime, whereas cooling to cryogenic temperatures increases the intensity, lifetime, and vibronic resolution. The binary adduct exhibits a drastically shorter phosphorescence lifetime of 6.7 ms versus free naphthalene (2.4 s) in a frozen dichloromethane matrix, which results from the external heavy-atom effect of silver. Adduct **1** represents a new class of phosphors containing lighter but more benign silver than mercury atoms in trinuclear d^{10} π-acid complexes as arene triplet sensitizers.

Pyrazolate ligands play an important role in the chemistry of monovalent trinuclear coinage metals [i.e., copper(I), silver(I), and gold(I)].[1] Depending on the steric demand and electronic properties of the substituents on the pyrazolyl moiety, metal pyrazolates assume structures that range from trimers, tetramers, hexamers, to polymers.[1] Part of our recent activities concern structural and spectroscopic properties of coinage metal complexes featuring fluorinated pyrazolyl ligands.[2−5] Synthesis of the first trinuclear gold(I) complex based on the fluorinated pyrazolate [3,5-$(CF_3)_2$Pz]$^-$ was reported by Bonati, Minghetti, and co-workers,[6] whereas the copper(I) and silver(I) congeners {[3,5-$(CF_3)_2$Pz]Cu}$_3$ and {[3,5-$(CF_3)_2$Pz]Ag}$_3$ were subsequently reported by Dias et al.[7] We have uncovered remarkable photophysical properties (including luminescence thermochromism, rigidochromism, and solvatochromism even in one compound, tunable multicolor phosphorescence by varying the metal or pyrazolate substituents, etc.), bonding trends (including localized or extended ground-state M···M metallophilic and excited-state M−M excimeric bonding), and π acid−base/donor−acceptor chemistry of these trinuclear d^{10} pyrazolates with relevance to a variety of optoelectronic applications.[2−5,8−12]

There is interest in the development of arene-based phosphors as possible new emitting materials for organic light-emitting diodes (OLEDs) with predictable emission colors.[13] A strategy to sensitize the T_1 triplet-state emission of arenes relies on complexation of the arenes with trinuclear

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(1) La Monica, G.; Ardizzoia, G. A. *Prog. Inorg. Chem.* **1997**, *46*, 151.

(2) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Palehepitiya Gamage, C. S.; Dias, H. V. R. *Inorg. Chem.* **2005**, *44*, 8200.

(3) Dias, H. V. R.; Diyabalanage, H. V. K.; Eldabaja, M. G.; Elbjeirami, O.; Rawashdeh-Omary, M. A.; Omary, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 7489.

(4) Dias, H. V. R.; Diyabalanage, H. V. K.; Rawashdeh-Omary, M. A.; Franzman, M. A.; Omary, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 12072.

(5) Dias, H. V. R.; Diyabalanage, H. V. K. *Polyhedron* **2006**, *25*, 1655.

(6) (a) Bovio, B.; Bonati, F.; Banditelli, G. *Inorg. Chim. Acta* **1984**, *87*, 25. (b) Banditelli, G.; Bandini, A. L.; Bonati, F.; Goel, R. G.; Minghetti, G. *Gazz. Chim. Ital.* **1982**, *112*, 539.

(7) Dias, H. V. R.; Polach, S. A.; Wang, Z. *J. Fluorine Chem.* **2000**, *103*, 163.

(8) Dias, H. V. R.; Gamage, C. S. P.; Keltner, J.; Diyabalanage, H. V. K.; Omari, I.; Eyobo, Y.; Dias, N. R.; Reohhr, N.; Mckinney, L.; Poth, T. *Inorg. Chem.* **2007**, *46*, 2979.

(9) Grimes, T.; Omary, M. A.; Dias, H. V. R.; Cundari, T. R. *J. Phys. Chem. A* **2006**, *110*, 5823.

(10) Tekarli, S. M.; Cundari, T. R.; Omary, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 1669.

(11) Vorontsov, I. I.; Kovalevsky, A. Yu.; Chen, Y.-S.; Graber, T.; Novozhilova, I. V.; Omary, M. A.; Coppens, P. *Phys. Rev. Lett.* **2005**, *94*, 193003.

(12) (a) Omary, M. A.; Rawashdeh-Omary, M. A.; Diyabalanage, H. V. K.; Dias, H. V. R. *Inorg. Chem.* **2003**, *42*, 8612. (b) Dias, H. V. R.; Diyabalanage, H. V. K.; Palehepitiya Gamage, C. S. *Chem. Commun.* **2005**, 1619. (c) Krishantha, D. M. M.; Palehepitiya Gamage, C. S.; Schelly, Z. A.; Dias, H. V. R. *Inorg. Chem.* **2008**, *47*, 7065.

(13) (a) Omary, M. A.; Kassab, R. M.; Haneline, M. R.; Elbjeirami, O.; Gabbaï, F. P. *Inorg. Chem.* **2003**, *42*, 2176. (b) Buress, C.; Elbjeirami, O.; Gabbaï, F. P.; Omary, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 12166. (c) Burress, C. N.; Bodine, M. I.; Elbjeirami, O.; Reibenspies, J. H.; Omary, M. A.; Gabbaï, F. P. *Inorg. Chem.* **2007**, *46*, 1388. (d) Elbjeirami, O.; Burress, C. N.; Gabbaï, F. P.; Omary, M. A. *J. Phys. Chem. C* **2007**, *111*, 9522.

(14) (a) Mohamed, A. A.; Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr. *Dalton Trans.* **2005**, 2597. (b) Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Fackler, J. P. *Coord. Chem. Rev.* **2005**, *249*, 1372.

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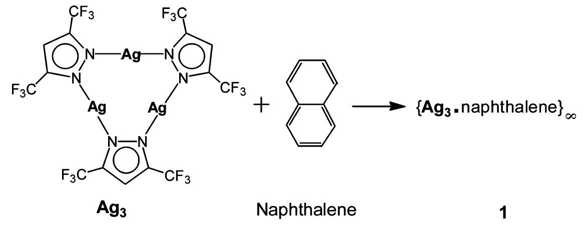
Chart 1



d^{10} complexes, which act as heavy-atom inducers in the resulting binary π-acid−base sandwich adducts that assemble into extended columnar stacks of alternating fluorinated and nonfluorinated molecules.[13,14] Gabbaï, Omary, and coworkers have reported this phenomenon upon π complexation of polycyclic aromatic organic molecules to the trimeric perfluoro-*o*-phenylenemercury(II) complex $[Hg(o\text{-}C_6F_4)]_3$, leading to intense $T_1 \rightarrow S_0$ arene monomer phosphorescence with a remarkable reduction of the triplet lifetime by up to 5 orders of magnitude.[13] Because $\{[3,5\text{-}(CF_3)_2Pz]M\}_3$ species exhibit similar chemistry, particularly when M = Ag,[2,8,10] it is desirable to replace mercury with a more benign metal such as silver in the fluorinated trimer that complexes to the electron-rich arene. Meanwhile, Dias et al. have recently isolated sandwiched supramolecular stacks of $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ with electron-rich π systems like benzene, toluene, and mesitylene.[15] Thus, here we report a natural extension of these literature precedents[2,10,13−15] to demonstrate the sensitization of arene monomer phosphorescence in a binary adduct of $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ (**Ag_3**) with a luminescent arene (naphthalene) to form **1**.

Synthesis of **1** was accomplished by the mixing of a hexane solution of **Ag_3** with a dichloromethane solution of naphthalene (Chart 1). This mixture was kept at 5 °C for several days to obtain X-ray-quality single crystals in 90% yield. **1** is an air-stable compound with a melting point of 262 °C. Synthetic and characterization details are given in the Supporting Information.

In order to investigate the extent of binary stacking between the arene and **Ag_3** in solution, fluorescence spectroscopy was used. The naphthalene monomer fluorescence intensity drops continuously upon submolar addition of **Ag_3** in CH_2Cl_2. The intermolecular deactivation (quenching) of the S_1 state of the aromatic compound is most likely a result of the enhanced intersystem crossing rate caused by a silver external heavy-atom effect, which is similar to the mercury heavy-atom effect reported earlier.[13] Fluorescence quenching data provide strong evidence for complexation of the aromatic molecule by **Ag_3** in solution. Thus, the kinetics of a Stern−Volmer analysis[16] yields a K_{SV} value of 94 ± 5 M^{-1} for adduct formation in solution (Figure 1). The magnitude of this constant is smaller than that for solution complexation of naphthalene with $[Hg(o\text{-}C_6F_4)]_3$ ($K_{SV} = 159 \pm 6\ M^{-1}$),[13c] consistent with the smaller atomic number and thus smaller spin−orbit constant of Ag ($\xi_{4d} = 1830\ cm^{-1}$) vs Hg ($\xi_{5d} = 4270\ cm^{-1}$).[17] The quenching observed is static, rather than dynamic, because of constant lifetimes during the titration (Figure 1).[16] Static quenching suggests a ground-state complex, $\{$**Ag_3**$\cdot$naphthalene$\}$, in solution, although the curvature at high concentration perhaps suggests a greater association to form more extended oligomers.[12c]

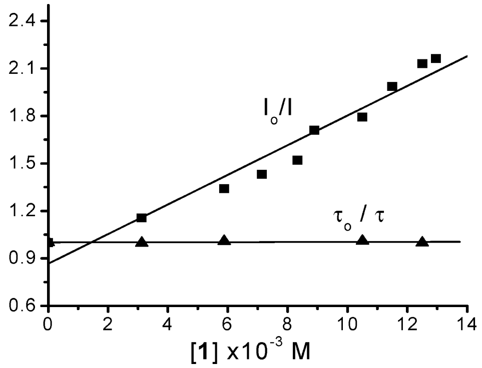


Figure 1. Stern−Volmer plots for the fluorescence quenching of naphthalene with **Ag_3**.

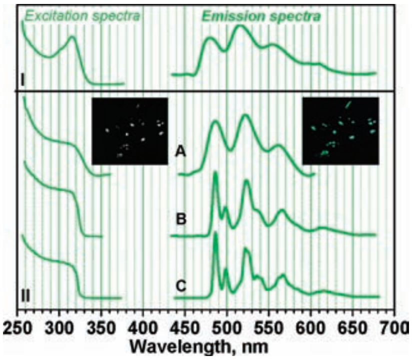


Figure 2. Photoluminescence excitation and emission spectra of frozen solution of equimolar amount **Ag_3** and naphthalene (I), and crystals of binary adduct **1** (II) at 298 K (A), 77 K (B), and 4 K (C).

The photoluminescence spectra of frozen CH_2Cl_2 solutions containing equimolar amounts of **Ag_3** and naphthalene exhibit only a green emission with a structured profile, assigned to naphthalene monomer phosphorescence (Figure 2). The naphthalene T_1 emission is drastically enhanced in the presence of silver centers in **Ag_3** because of spin−orbit coupling (external heavy-atom effect). Crystals of **1** exhibit the same emission profile due to the naphthalene T_1 state even at room temperature (RT; see Figure 2). At cryogenic temperatures, the intensity and vibronic resolution are enhanced, as expected because of inhibition of the nonradiative depopulation of the emitting T_1 state upon cooling. The excitation bands for solid **1** are red-shifted from the absorption bands of the free **Ag_3** and naphthalene components,[2,16] suggesting a charge-transfer excitation route (promoted by acid−base electrostatic attraction), as proposed in literature precedents with Au_3 and Hg_3 triplet sensitizers.[13d,14] The vibronic energies correspond reasonably well to those known for naphthalene monomer phosphorescence.[16] Two progressions are identified from the highest-resolution data

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[15] Dias, H. V. R.; Gamage, C. S. P. *Angew. Chem., Int. Ed.* **2007**, 2192.

[16] Lakowicz, J. *Principles of Fluorescence Spectroscopy*; Kluwer/Plenum: New York, 1999.

[17] See, for example: (a) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2006. (b) Griffith, J. S. *Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1964.

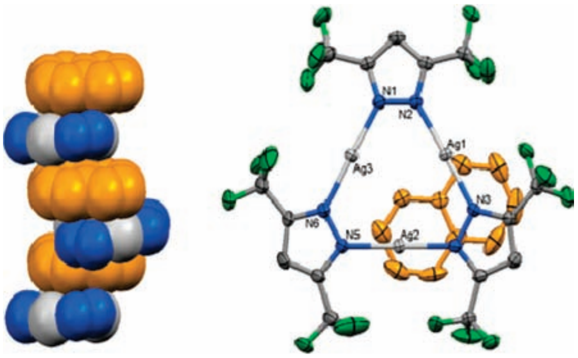

Figure 3. Crystal structure of {**Ag_3**·naphthalene}$_\infty$ showing the repeating unit (right, with hydrogen atoms omitted for clarity) and a binary stack (left; only C atoms of naphthalene and N and Ag atoms of **Ag_3** are shown).

for solid **1** at 4 K, corresponding to naphthalene ring stretching and bending modes at 1421 ± 35 and 530 ± 13 cm^{-1}, respectively, whereas only the former (1375 ± 62 cm^{-1}) is discernible at RT; see Table S2 (Supporting Information) for further details. The frozen-solution measurements in CH_2Cl_2 at 77 K reveal shortening of the naphthalene phosphorescence lifetime upon complexation to **Ag_3** by 3 orders of magnitude, $\tau^P = 6.700 \pm 0.095$ ms for **1** vs 2.4 s for naphthalene. This acceleration of the T_1 phosphorescence along with the complete quenching of the S_1 fluorescence of naphthalene accentuates the heavy-atom effect in the presence of **Ag_3**.

The X-ray structure of {**Ag_3**·naphthalene}$_\infty$ is shown in Figure 3. This adduct exists as an extended binary stack consisting of alternating **Ag_3** and naphthalene moieties. The shortest Ag−C(naphthalene) distance is 3.00 Å. This distance is well within the summed van der Waals radii of Ag and C (3.42 Å) and is significantly shorter than the shortest Hg−C(naphthalene) distance of 3.25 Å in the analogous {[Hg(*o*-C_6F_4)]$_3$·naphthalene}$_\infty$ stacks reported by the Gabbaï group.[18] There are several close (<3.42 Å) contacts with two silver atoms of each of the sandwiching **Ag_3** units on either side of the naphthalene molecule. Therefore, the naphthalene molecules in the stacks of {**Ag_3**·naphthalene}$_\infty$ form relatively strong interactions with **Ag_3** units, consistent with the photophysical results.

Further assessment of the amount of the external heavy-atom effect induced by **Ag_3** in the solid state was carried out by analyzing the kinetics of the radiative decay. The phosphorescence lifetimes for solid **1** at RT, 77 K, and 4 K yielded $\tau = 830 \pm 10$, 2592 ± 55, and 7293 ± 89 μs, respectively. These solid-state lifetimes of **1**, like the CH_2Cl_2 frozen-solution values above, are much shorter than the reported monomer phosphorescence lifetimes of free naphthalene in EPA glass or CH_2Cl_2 frozen solution.[13] Temperature-dependent lifetime measurements allow the separation of radiative (k_r) and nonradiative (k_{nr}) decay rate constants because k_{nr} vanishes exponentially at temperatures approaching 0 K.[19] Least-squares analysis to fit the experimental data of $1/\tau$ vs $1/T$ (see the Supporting Information) attains quantitative evaluation of the parameters k_r, k_o, and E_a for the solid adduct **1** using known treatments.[13,19] This analysis yields $k_r = 1.37\ (0.06) \times 10^2\ s^{-1}$ and $E_a = 0.54$ kJ/mol. Using the derived k_r with the lifetime data attains phosphorescence quantum yield values of 15%, 45%, and 100% at RT, 77 K, and 4 K, respectively, for solid **1**. Table 1 summarizes the photophysical parameters extracted via this analysis.

Table 1. Photophysical Parameters for Solid **1**

				k_{nr} (s^{-1})		
k_r (s^{-1})	ϕ_{RT} (%)	$\phi_{77\ K}$ (%)	$\phi_{4\ K}$ (%)	RT	77 K	4 K
137	15.0	45.0	100	1040	235	5.35×10^{-6}

The lower phosphorescence quantum yield at RT for **1** compared to the naphthalene adduct of [Hg(*o*-C_6F_4)]$_3$, ϕ_{RT} = 54%,[13] is consistent with the smaller heavy-atom effect imposed by silver centers compared to mercury. Thus, there will be a tradeoff if one wishes to use a silver Lewis acidic trimer as a more benign alternative to a mercury trimer for lighting applications. Further enhancement of the phosphorescence quantum yield can perhaps be achieved by improving the size match to attain better stacking between the arenes and **Ag_3** (e.g., by using larger polycyclic aromatic fluorophores). On the other hand, the near-millisecond lifetimes of naphthalene adducts with both Ag_3 and Hg_3 complexes are not desirable for OLED applications because of the increased chance of triplet−triplet annihilation events, as known for lanthanide complexes. Expansion of this work to *N*-heterocyclic or heavy-atom-substituted arenes may alleviate this problem, as has been demonstrated for Hg_3 complexes.[13b,d]

In conclusion, the studies herein indicate π complexation of naphthalene to {[3,5-$(CF_3)_2$Pz]Ag}$_3$ in both the solid state and solution, as reflected by fluorescence quenching in fluid solutions and phosphorescence sensitization in the solid state and frozen solutions concomitant with a 3-order-of-magnitude reduction of the triplet lifetime versus free naphthalene. Current efforts are focused on the synthesis of luminescent binary adducts with improved size match, versatile emission colors, and quantum yields of the substrate emission toward incorporating the resulting materials in optoelectronic devices or using them as luminescent sensors.

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Supporting Information Available: X-ray crystallographic data for **1** (CIF) and additional synthetic, characterization, and spectral details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Haneline, M. R.; Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 3737.

(19) (a) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer: Berlin, 1994. (b) Shepherd, N.; Holloway, P. H. Zinc Sulphide. In *Handbook of Electroluminescent Materials*; Vij, D. R., Ed.; Institute of Physics Publishing: London, 2004; Chapter 2.