Blue-Emitting Dinuclear N-heterocyclic Dicarbene Gold(I) Complex Featuring a Nearly Unit Quantum Yield

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S Supporting Information

ABSTRACT: Dinuclear N-heterocyclic dicarbene gold(I) complexes of general formula $[Au_2(RIm-Y-ImR)_2](PF_6)_2$ (R = Me, Cy; Y = $(CH_2)_{1-4}$, o-xylylene, m-xylylene) have been synthesized and screened for their luminescence properties. All the complexes are weakly emissive in solution whereas in the solid state some of them show significant luminescence intensities. In particular, crystals or powders of the complex with R = Me, Y = $(CH_2)_3$ exhibit an intense blue emission (λ_{max} = 450 nm) with a high quantum yield (Φ_{em} = 0.96). The X-ray crystal structure of this complex is characterized by a rather short intramolecular Au⋯Au distance (3.272 Å). Time dependent density functional theory (TDDFT) calculations have been used to calculate the UV/vis properties of the ground state as well as of the first excited state of the complex, the latter featuring a significantly shorter Au⋯Au distance.
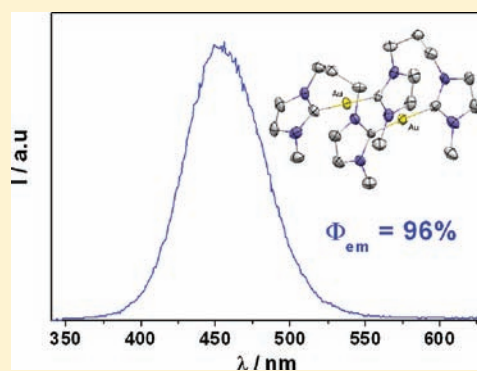
INTRODUCTION

In the past decade, there has been an enormously increasing interest in gold chemistry, with applications spanning from homogeneous or heterogeneous catalysis to materials science, nanotechnology, and biomedicine.[1] Focusing on gold(I) complexes, several studies have dealt with their photophysical properties, which are often put into relation with the so-called aurophilic interaction.[2] The term "aurophilicity" has been introduced by Schmidbaur in the early 1990s to describe the weak interaction between linearly coordinated Au(I) closed-shell centers (electronic configuration $5d^{10}$).[3] These inter-actions, by means of relativistic effects, lead to a mixing of the gold 5d and 6s orbitals, lowering the energy gap between the ground and excited states and enhancing the probability of electronic transitions.[4] For example, it has been demonstrated that the presence of aurophilic interactions significantly influences the luminescence properties exhibited by phosphino or diphosphino gold(I) complexes.[5]

Since their first appearance, N-heterocyclic carbene ligands (NHCs)[6] have been considered an alternative to phosphines because of their strong σ-donor abilities. Moreover, recently Pyykkö et al. have investigated with computational methods the effect of neutral ligands on the aurophilic interaction in complexes of general formula $[ClAuL]_2$ and have predicted that NHC ligands would yield the strongest metal–metal interaction.[7] In light of the above, it is not surprising that in the last years several reports on the luminescence properties of mono- and especially polynuclear gold(I) complexes with NHC ligands have been published. However, despite the diverse nature of the investigated systems (mono- and dinuclear complexes, higher nuclearity clusters, heteropolymetallic complexes)[8−10] only few structures with clearly outstanding emission characteristics (tunable emission and near-unity quantum yields) in the solid state, which is the relevant state for technological applications, have emerged up to now.[9,10] Moreover, even in these cases the complexes have been found to be highly emissive only as single crystals, as their luminescence depends on the molecular stacking in the lattice.[9]

In the past years, we have been interested in the synthesis of poly-NHC complexes of late transition metals (Pd(II), Pt(II), Cu(I), Ag(I)).[11] We report here on the extension of those studies to gold(I) dicarbene complexes, aimed at establishing a correlation between the structure of the dicarbene ligand

(length and flexibility of the bridge between the carbene units) and the luminescence properties of the corresponding complexes. This effort has eventually led to the identification of a complex with exceptional photoluminescence properties.

■ EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased by Aldrich as high-purity products and generally used as received; all solvents were used as received as technical grade solvents. The diimidazolium salts 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide,[12] 1,1′-dimethyl-3,3′-ethylenediimidazolium dibromide,[13] 1,1′-dimethyl-3,3′-propylenediimidazolium dibromide,[14] 1,1′-dimethyl-3,3′-butylenediimidazolium dibromide,[14] 1,1′-dimethyl-3,3′-(m-xylylene)diimidazolium dibromide,[15] 1,1′-dimethyl-3,3′-(o-xylylene)diimidazolium dibromide,[15] and 1,1′-dicyclohexyl-3,3′-methylenediimidazolium dibromide[16] were prepared according to literature procedures.

NMR spectra were recorded on a Bruker Avance 300 MHz (300.1 MHz for ^{1}H and 75.5 for ^{13}C); chemical shifts (δ) are reported in units of parts per million (ppm) relative to the residual solvent signals.

General Procedure for the Synthesis of Gold(I) Complexes (1-Br)-(7-Br). A mixture of sodium acetate (1.80 mmol), the diimidazolium salt (0.80 mmol), and AuCl(SMe₂) (0.81 mmol) in dimethylformamide (DMF, 25 mL) was heated and maintained at 120 °C for 2 h. Addition of n-hexane (10 mL) and dichloromethane (1 mL) afforded a white solid, which was filtered and dried under vacuum, and used for the subsequent step without further purification.

Bis(1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)-digold(I) Dibromide (1-Br). White solid (yield 87%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.89 (s, 12H, CH₃), 6.41 (d AB system, $^2J_{HH}$ = 12.6 Hz, 2H, CH₂), 7.25 (d AB system, $^2J_{HH}$ = 12.6 Hz, 2H, CH₂), 7.61 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH), 8.02 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 38.0 (CH₃), 61.8 (CH₂), 121.8 (CH), 124.8 (CH), 183.2 (NCN).

Bis(1,1′-dimethyl-3,3′-ethylenediimidazol-2,2′-diylidene)digold(I) Dibromide (2-Br). White solid (yield 90%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.78 (s, 12H, CH₃), 4.81 (s, 8H, CH₂), 7.45 (m, 8H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 38.7 (CH₃), 49.9 (CH₂), 122.5 (CH), 123.3 (CH), 182.7 (NCN).

Bis(1,1′-dimethyl-3,3′-propylenediimidazol-2,2′-diylidene)digold-(I) Dibromide (3-Br). White solid (yield 92%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 2.60 (m, 4H, CH₂), 3.50 (s, 12H, CH₃), 4.17 (m, 8H, CH₂N), 7.62 (s, 4H, CH), 7.76 (s, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 30.7 (CH₂), 36.7 (CH₃), 46.3 (NCH₂), 121.3 (CH), 124.4 (CH), 181.9 (NCN).

Bis(1,1′-dimethyl-3,3′-butylenediimidazol-2,2′-diylidene)digold(I) Dibromide (4-Br). White solid (yield 96%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 1.85 (m, 8H, CH₂), 3.81 (s, 12H, CH₃), 4.21 (m, 8H, CH₂N), 7.52 (s, 4H, CH), 7.56 (s, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 28.3 (CH₂), 37.5 (CH₃), 49.9 (NCH₂), 122.2 (CH), 123.4 (CH), 182.6 (NCN).

Bis(1,1′-dicyclohexyl-3,3′-methylenediimidazol-2,2′-diylidene)-digold(I) Dibromide (5-Br). White solid (yield 96%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 1.00−2.00 (m, 40H, CH₂−Cy), 4.46 (s, 4H, CH-Cy), 6.43 (d AB system, $^3J_{HH}$ = 13.8 Hz, 2H, CH₂), 7.12 (d AB system, $^2J_{HH}$ = 13.8 Hz, 2H, CH₂), 7.82 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH), 7.96 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 24.4 (CH₂ Cy), 24.9 (CH₂ Cy), 25.0 (CH₂ Cy), 33.1 (CH₂ Cy), 33.4 (CH₂ Cy), 61.1 (CH Cy), 62.6 (CH₂), 120.5 (CH), 122.2 (CH), 181.5 (NCN).

Bis(1,1′-dimethyl-3,3′-(m-xylylene)diimidazol-2,2′-diylidene)-digold(I) Dibromide (6-Br). White solid (yield 93%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.43 (s, 12H, CH₃), 5.30 (s, 8H, CH₂), 7.33 (m, 8H, xylylen), 7.54 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH), 7.61 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH). The ^{1}H NMR spectrum is in agreement with that reported in the literature.[17]

Bis(1,1′-dimethyl-3,3′-(o-xylylene)diimidazol-2,2′-diylidene)-digold(I) Dibromide (7-Br). White solid (yield 95%). ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.76 (s, 12H, CH₃), 5.68 (s, 8H, CH₂),

6.71 (s, 4H, CH), 7.23 (m, 4H, CH), 7.58 (m, 8H, xylylen). The ^{1}H NMR spectrum is in agreement with that reported in the literature.[17]

General Procedure for the Synthesis of Gold(I) Complexes (1-PF₆)-(7-PF₆). The dibromide complex (0.3 mmol) was dissolved in methanol (10 mL), and a solution of KPF₆ (5 equiv.) in water (3 mL) was added, affording the precipitation of the desired product. The solid was filtered, washed with H₂O (3 mL), methanol (2 × 3 mL), and finally dried under vacuum.

Bis(1,1′-dimethyl-3,3′-methylenediimidazol-2,2′-diylidene)-digold(I) Dihexafluorophosphate (1-PF₆). White solid (yield 73%). Anal. Calcd for C₁₈H₂₄Au₂F₁₂N₈P₂: C, 20.86; H, 2.33; N, 10.81%. Found: C, 21.15; H, 2.30; N, 10.23%. ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.88 (s, 12H, CH₃), 6.33 (d AB system, 2H, CH₂), 7.18 (d AB system, 2H, CH₂), 7.60 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH), 7.89 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH). ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 3.86 (s, 12H, CH₃), 6.08 (d AB system, 2H, CH₂), 6.92 (d AB system, 2H, CH₂), 7.27 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH), 7.50 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 38.0 (CH₃), 61.8 (CH₂), 121.8 (CH), 124.8 (CH), 183.2 (NCN). ^{13}C NMR (CD₃CN, 25 °C, ppm): δ = 39.2 (CH₃), 63.6 (CH₂), 122.3 (CH), 125.5 (CH), 185.3 (NCN).

Bis(1,1′-dimethyl-3,3′-ethylenediimidazol-2,2′-diylidene)digold(I) Dihexafluorophosphate (2-PF₆). White solid (yield 70%). Anal. Calcd for C₂₀H₂₈Au₂F₁₂N₈P₂: C, 22.57; H, 2.65; N, 10.52%. Found: C, 22.77; H, 2.61; N, 9.90%. ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.78 (s, 12H, CH₃), 4.79 (s, 8H, CH₂), 7.39 (d, $^3J_{HH}$ = 1.5 Hz, 4H, CH), 7.44 (d, $^3J_{HH}$ = 1.5 Hz, 4H, CH). ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 3.73 (s, 12H, CH₃), 4.73 (s, 8H, CH₂), 7.07 (d, $^3J_{HH}$ = 1.4 Hz, 4H, CH), 7.11 (d, $^3J_{HH}$ = 1.4 Hz, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 38.6 (CH₃), 59.8 (CH₂), 123.3 (CH), 124.6 (CH), 183.5 (NCN).

Bis(1,1′-dimethyl-3,3′-propylenediimidazol-2,2′-diylidene)digold-(I) Dihexafluorophosphate (3-PF₆). White solid (yield 78%). Anal. Calcd for C₂₂H₃₂Au₂F₁₂N₈P₂: C, 24.19; H, 2.95; N, 10.26%. Found: C, 24.48; H, 2.98; N, 9.25%. ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 2.54 (m, 4H, CH₂), 3.53 (s, 12H, CH₃), 4.23 (m, 8H, CH₂N), 7.24 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH), 7.30 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH). ^{13}C NMR (CD₃CN, 25 °C, ppm): δ = 30.0 (CH₂), 38.0 (CH₂N), 48.0 (CH₃), 121.8 (CH), 125.0 (CH), 184.1 (NCN).

Bis(1,1′-dimethyl-3,3′-butylenediimidazol-2,2′-diylidene)digold(I) Dihexafluorophosphate (4-PF₆). White solid (yield 61%). Anal. Calcd for C₂₄H₃₆Au₂F₁₂N₈P₂: C, 25.73; H, 3.24; N, 10.00%. Found: C, 25.36; H, 3.00; N, 9.18%. ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 1.89 (m, 8H, CH₂), 3.79 (s, 12H, CH₃), 4.18 (m, 8H, CH₂N), 7.17 (d, $^3J_{HH}$ = 1.0 Hz, 8H, CH). ^{13}C NMR (CD₃CN, 25 °C, ppm): δ = 29.3 (CH₂), 38.5 (CH₃), 51.3 (NCH₂), 122.7 (CH), 124.0 (CH), 184.8 (NCN).

Bis(1,1′-dicyclohexyl-3,3′-methylenediimidazol-2,2′-diylidene)-digold(I) Dihexafluorophosphate (5-PF₆). White solid (yield 62%). Anal. Calcd for C₃₈H₅₆Au₂F₁₂N₈P₂: C, 34.87; H, 4.31; N, 8.56%. Found: C, 33.87; H, 4.23; N, 7.80%. ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 1.00−2.00 (m, 40H, CH₂−Cy), 4.47 (br, 4H, CH-Cy), 6.38 (AB system, 2H, CH₂), 7.09 (AB system, 2H, CH₂), 7.80 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH), 7.90 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH). ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 1.00−2.00 (m, 40H, CH₂−Cy), 4.44 (br, 4H, CH-Cy), 6.11 (d AB system, 2H, CH₂), 6.87 (d AB system, 2H, CH₂), 7.35 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH), 7.48 (d, $^3J_{HH}$ = 1.0 Hz, 4H, CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 24.4 (CH₂ Cy), 25.0 (CH₂ Cy), 25.1 (CH₂ Cy), 33.1 (CH₂ Cy), 33.5 (CH₂ Cy), 61.1 (CH Cy), 62.6 (CH₂), 120.6 (CH), 122.1 (CH), 181.5 (NCN).

Bis(1,1′-dimethyl-3,3′-(m-xylylene)diimidazol-2,2′-diylidene)-digold(I) Dihexafluorophosphate (6-PF₆). White solid (yield 61%). Anal. Calcd for C₃₂H₃₆Au₂F₁₂N₈P₂: C, 31.59; H, 2.98; N, 9.21%. Found: C, 32.12; H, 2.84; N, 8.73%. ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.52 (s, 12H, CH₃), 5.30 (s, 8H, CH₂), 7.33 (m, 8H, xylylen), 7.53 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH), 7.60 (d, $^3J_{HH}$ = 1.2 Hz, 4H, CH). ^{1}H NMR (CD₃CN, 25 °C, ppm): δ = 3.53 (s, 12H, CH₃), 5.20 (s, 8H, CH₂), 7.00−7.40 (m, 16H, xylylen).

Bis(1,1′-dimethyl-3,3′-(o-xylylene)diimidazol-2,2′-diylidene)-digold(I) Dihexafluorophosphate (7-PF₆). White solid (yield 68%). Anal. Calcd for C₃₂H₃₆Au₂F₁₂N₈P₂: C, 31.58; H, 2.98; N, 9.21%. Found: C, 33.66; H, 2.88; N, 10.01%. ^{1}H NMR (CD₃CN, 25 °C,

ppm): δ = 3.80 (s, 12H, CH$_3$), 5.61 (s, 8H, CH$_2$), 6.43 (s, 4H, CH), 6.85 (s, 4H, CH), 7.63 (m, 8H, xylylen). ^{13}C NMR (CD$_3$CN, 25 °C, ppm): δ = 38.6 (CH$_3$), 53.5 (CH$_2$), 121.5 (CH), 123.7 (CH), 131.4 (CH), 134.1 (CH), 134.8 (C), 185.1 (NCN).

X-ray Structure Determination of (3-PF$_6$). Data for complex **3-PF$_6$** were collected at 173 K on a Bruker APEX II single-crystal diffractometer, using Mo–Kα graphite monocromated radiation (λ = 0.71073 Å) and equipped with an area detector.[18] Crystal data: hexagonal, space group = P3212, a = 12.0147(7), b = 12.0147(7), c = 19.406(2), V = 2426.0(4) Å^3, Z = 3, μ = 9.258 mm^{-1}, ρ = 2.243 g cm^{-3}, Unique reflections: 4984 (R_{int} =0.0487), Final R = 0.0260, Rw = 0.0569, GOF = 1.009. The structure was solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[19] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in the ideal geometrical positions.

Crystallographic data for compound **3-PF$_6$** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 835523 (data at room temperature (RT)) and 855138 (data at 173 K). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

Spectroscopic Measurements. Absorption spectra were recorded with a Perkin-Elmer λ950 or λ650 spectrophotometer. For luminescence experiments, the samples in solution were placed in fluorimetric 1-cm path cuvettes and, when necessary, purged from oxygen by bubbling with argon, while the solid state samples (powder) were placed in between two quartz disks fixed by a dedicated metal pincer. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm). A Xe900 450 W xenon arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby[20] using air-equilibrated ([Ru(bpy)$_3$]Cl$_2$ in water solution, Φ_{em} = 0.028)[21] as standard.

Emission lifetimes in the ns-μs range were determined with the single photon counting technique by means of the same Edinburgh FLS920 spectrometer using a laser diode as excitation source (1 MHz, λ_{exc} = 407 nm, 200 ps time resolution after deconvolution) and the above-mentioned PMTs as detectors, or with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the range 2–40 kHz (λ_{exc} = 337 nm, 0.5 ns time resolution) or by using pulsed NanoLED excitation sources at 278 nm, 331 nm, 465 nm, and 560 nm (pulse width ≤0.3 ns); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237–01 photomultiplier tube. Analysis of the luminescence decay profiles versus time was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer.

To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar, filled up with liquid nitrogen. For solid samples, Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulfate coated integrating sphere (4 or 6 in.), a He–Cd laser (λ_{exc}: 325 nm, 5mW) or a 450W Xe lamp (λ_{exc} = tunable by a monochromator supplied with the instrument) as light sources, and a R928 photomultiplayer tube or a CCD AVA-Spec2048 as signal detectors, following the procedure described by De Mello et al.[22] Experimental uncertainties are estimated to be ±8% for lifetime determinations, ±20% for emission quantum yields, and ±2 nm and ±5 nm for absorption and emission peaks, respectively.

Computational Details. The PBE0 functional was used in all the calculations,[23] which have been performed with the Gaussian09 set of programs.[24] The electronic configuration of the molecular systems was described by the standard TZVP basis set of Ahlrichs and co-workers for H, C, and N.[25] For Au we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential (standard SDD basis set in Gaussian09) basis set, with the associated triple-ζ valence basis set.[26]

All the time dependent density functional theory (TDDFT) calculations were focused on singlet excited states. Both the DFT and TDDFT geometry optimization of the singlet ground state and of the singlet first excited state were performed without symmetry constraints. Solvent effects, based on the polarizable continuum solvation model PCM using acetonitrile as a solvent, were used in both geometry optimization and in the calculation of the adsorption and emission spectra.[27] The atomic contribution of single atoms to the molecular orbitals was performed in the framework of Mulliken population analysis.

■ RESULTS AND DISCUSSION

The gold(I) dicarbene complexes **1-Br−7-Br** have been synthesized by direct metalation of the corresponding diazolium salt, in the presence of a mild base (NaOAc), with a suitable Au(I) precursor (AuCl(SMe$_2$)), following a procedure already reported by Baker[8f,17] and Hemmert.[8c] The subsequent anionic metathesis with KPF$_6$, in a water−methanol mixture, afforded the complexes **1-PF$_6$−7-PF$_6$** as analitically pure, white solids in good yields (Scheme 1).

Scheme 1. Synthesis of the Gold(I) Dicarbene Complexes 1−7^a
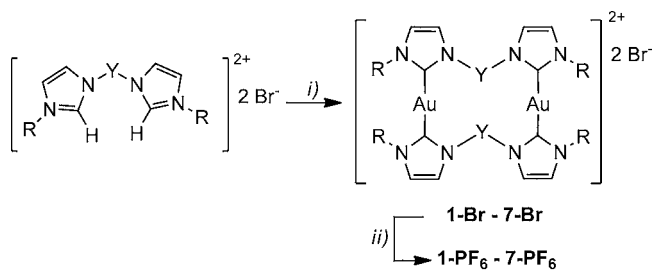
R = Me; **1**, Y = CH$_2$; **2**, Y = (CH$_2$)$_2$; **3**, Y = (CH$_2$)$_3$; **4**, Y = (CH$_2$)$_4$;
         6, Y = m-xylylene; **7**, Y = o-xylylene
R = Cy; **5**, Y = CH$_2$

^{a}Reagents and reaction conditions. (i) AuCl(SMe$_2$), NaOAc, DMF, 2 h; (ii) KPF$_6$, MeOH/H$_2$O.

The absence of the signal relative to the hydrogen atom in 2 position of the heterocyclic ring in the ^{1}H NMR spectrum of **1-PF$_6$−7-PF$_6$** is indicative of the deprotonation of the diimidazolium salt and, as a consequence, of the formation of the dicarbene complex. Moreover, the ^{1}H and ^{13}C NMR spectra present a limited number of sharp signals, indicating highly symmetrical structures. The presence of the gold−carbene bond is confirmed by the ^{13}C spectra, in which the carbene carbon resonance is located at about 180 ppm, in the range of similar carbene carbons bonded to gold(I) centers.[8c,f,17]

The Au(I) complexes have been photophysically investigated in solution and in solid state at both RT and low temperature (77 K). The absorption profiles in acetonitrile solution (Figure 1) are centered in the UV spectral window (ca. 220−320 nm) and can be attributed to π−π* ligand-centered (LC) transitions, although they are substantially red-shifted relative to those of the corresponding diimidazolium precursors (see the Supporting Information) because of the perturbation provided by the metal center.[8c]

All the complexes are stable in solution over weeks and, in acetonitrile, exhibit a relatively weak photoluminescence (Φ_{em} up to 0.4%). By contrast, in the solid state **3-PF$_6$**, **4-PF$_6$**, and **7-PF$_6$** show significant emission intensities (Φ_{em} = 96%, 7.2%, and 9.5%, respectively) at RT (as KBr discs) whereas the other complexes are almost nonemissive (Figure 2). The correspond-
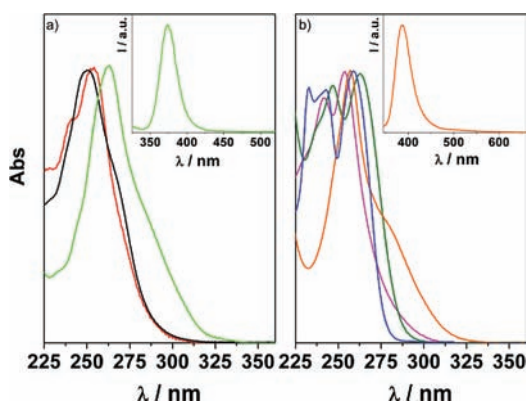
Figure 1. Normalized absorption spectra of (a) **1-PF₆** (Black), **2-PF₆** (Red), **3-PF₆** (Green) and (b) **4-PF₆** (Blue), **5-PF₆** (Magenta), **6-PF₆** (Dark green), **7-PF₆** (Orange) in CH₃CN. The emission profiles (λ_{exc} = 250 nm, O.D. = 0.2) of **3-PF₆** (Inset a) and **7-PF₆** (Inset b) in acetonitrile are reported as the strongest emitters of the series under these conditions.
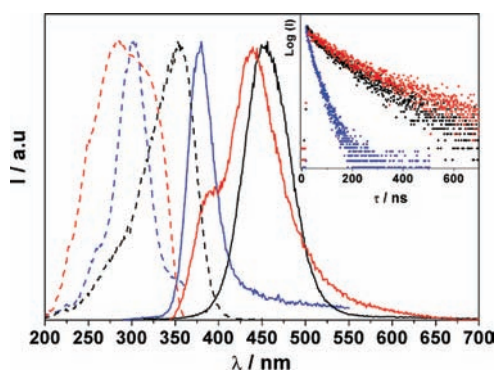

Figure 2. Main window: Normalized emission (solid line, $\lambda_{exc} = \lambda_{max}$) and excitation (dashed line, $\lambda_{em} = \lambda_{max}$) spectra of **3-PF₆** (black), **4-PF₆** (blue), and **7-PF₆** (red) in solid state (as KBr disk) at RT. The corresponding lifetime decays are reported in the inset (full circle, $\lambda_{exc} = \lambda_{max}$).

ing lifetimes (Figure 2, inset) are in the range of hundreds of nanoseconds (τ = 565, 132, and 770 ns, respectively).

Notably, whereas only one emission band is observed for complexes **3-PF₆** and **4-PF₆**, in the case of complex **7-PF₆** a shoulder is found. Bimodal emissions have been already observed with other gold(I)-NHC complexes and tentatively attributed to the simultaneous presence of LC and MC emissions.[8c] Incidentally, complex **7-PF₆** is the only emitting complex among those described herein which presents an aromatic system in the ligand structure.

The photophysical analysis performed on the diimidazolium salt precursors of the dicarbene ligands did not reveal any emission. This allows to rule out the presence of LC radiative transitions. This hypothesis is reinforced by the long lifetimes obtained for the Au(I) complexes in the solid state (see above), corroborating the assumption that aurophilic interactions can be responsible for such a highly efficient emission.[28]

The emission properties at low temperature (CH₃CN rigid matrix) have been also probed and the emission profiles of **3-PF₆** and **7-PF₆** are reported in the Supporting Information (with the other samples weak or no emission could be detected). Notably, the emission maxima of the complexes show differences upon changing the experimental environment. For instance, **3-PF₆** profiles are peaked at 374, 450, and 488 nm

in CH₃CN, RT solid state and 77 K rigid matrix, respectively. Such effect, given the absence of any LC luminescence by the salt precursors, might be related to a tuning of the Au···Au distance under different conditions (for example, in the crystalline state, the Au···Au distance is 3.2758 Å at RT and 3.2722 Å at 173 K).

Single-crystals of complex **3-PF₆**, suitable for X-ray diffraction, have been obtained upon diffusion of diethyl ether in an acetonitrile solution of **3-PF₆**. The ORTEP view of the cationic complex **3** is reported in Figure 3 together with the
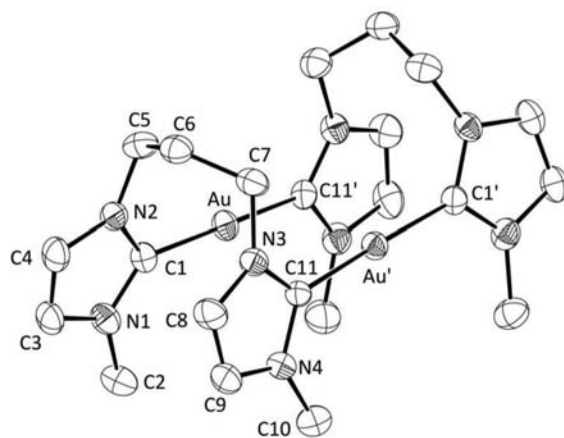

Figure 3. ORTEP drawing of complex **3**. PF₆⁻ anions have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1–Au 2.026(4), C1–N2 1.339(6), C1–N1 1.351(6), C11′–Au 2.023(4), C11–N4 1.323(6), C11–N3 1.366(6), Au···Au′ 3.2722(5); C1–Au–C11′ 177.59(16), N2–C1–N1 105.7(4), N2–C1–Au 128.1(3), N1–C1–Au 126.2(4), N4–C11–N3 105.5(4), N4–C11–Au 128.1(4), N3–C11–Au 126.3(3). Symmetry code for generating atoms: ′ = −x +y, y, −z+2/3.

atomic numbering scheme. A list of the most important bond distances and angles is reported in the caption. The X-ray diffraction (XRD) analysis shows a dinuclear structure, in which the two gold(I) centers are linearly dicoordinated, as expected for a heavy metal center in d¹⁰ configuration. The bond angles C_carbene−Au−C_carbene are in fact close to linearity (C1−Au1−C11 177.59(16)°) and the bond distances Au−C_carbene (2.025(4) Å) are comparable with those reported for analogous bis(NHC) gold(I) complexes.[8c,f,17,29]

The relatively short intramolecular Au···Au distance (3.2722(5) Å) is indicative of the presence of aurophilic interactions (range of Au···Au distance for aurophilic interactions 2.8−3.5 Å).[3] Notably, the Au···Au distance is significantly shorter than the one observed for complex **1** (3.5425(6) Å) bearing the methylene bridge.[17] The dinuclear complex **3-PF₆** is symmetric; one-half of the structure is correlated with the other half by a 2-fold axis. The propylenic linkers of the two bridging dicarbene ligands are arranged on the same side with respect to the mean plane defined by the gold and the carbene carbon atoms. The dihedral angle between the mean planes of the two imidazol-2-ylidene rings of the same bridging ligand is 16.29(2)°; the mean planes of the two imidazol-2-ylidene rings coordinated to the same Au atom are also slightly twisted (dihedral angle 11.51(2)°).

In the molecular packing, intermolecular π−π stacking interactions between the imidazol-2-ylidene rings of two dinuclear units are present (Figure 4); the centroid-centroid distance between the carbene rings is 3.814(4) Å. In the
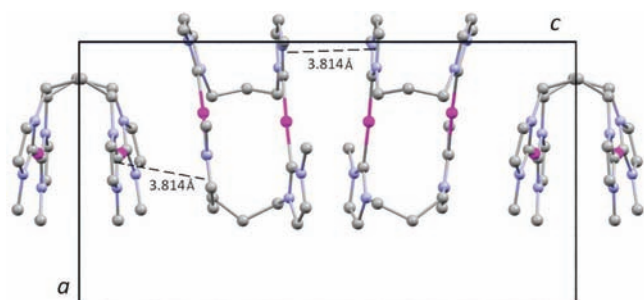
Figure 4. Crystal packing of complex **3**. (View along *b* axis). PF_6^- anions have been omitted for clarity. Au pink, N blue and C gray.

elemental crystallographic cell three dimeric units are present, arranged in a staggered way along the 3-fold screw axis. This arrangement produces a channel (Figure 5) which brings the gold atoms of vicinal complexes to a distance of 3.720(2) Å.
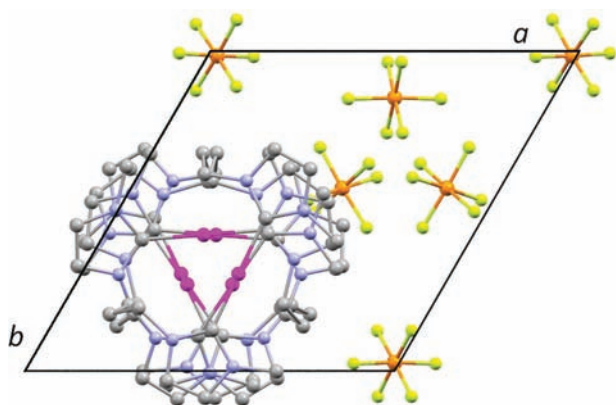

Figure 5. Crystal packing of complex **3-PF$_6$**. (View along *c* axis). Au, pink; N, blue; C, gray; P, orange; and F, yellow.

The exceptional quantum yield observed with **3-PF$_6$** in the solid state can be attributed to the peculiar arrangement of the complex molecules in the crystal, as it was the case with previously reported complexes,[9] or to a molecular property of **3-PF$_6$**. Basically the same luminescence is exhibited by a sample of **3-PF$_6$** both as a crystalline solid and as a powder. However, XRD analysis of the powder yields a pattern fully interpretable with microcrystalline **3-PF$_6$**. Therefore, although the use of single crystals is not necessary for achieving high emissions with **3-PF$_6$**, addditional investigations are needed to discriminate between the two hypotheses listed above.

To shed light on the nature of the transitions observed in the UV/vis spectra we performed TDDFT calculations on **3**. We started with the geometry optimization of the ground state as well as of the first singlet excited state of **3** in CH_3CN. In the ground state the optimized Au···Au distance is 3.35 Å, which is in good agreement with the experimental value of 3.27 Å. In the first excited state the Au···Au distance is predicted to be remarkably shorter, 2.80 Å. The Mayer bond order[30] between the Au centers increases from 0.17 in the ground state to 0.42 in the first excited state. Although it is difficult to know the accuracy of this prediction,[31] the extent of the reduction of the Au···Au distance, roughly 0.5 Å, and the corresponding increase in the Mayer bond order, roughly 0.2, are large enough to support the hypothesis of a sizable increase of the Au···Au interaction in the first excited state. TDDFT calculations on the ground state geometry indicate two intense bands at 277 and 252 nm, in good agreement with the experimental broad absorption band at roughly 260 nm. The former band involves a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), with the HOMO essentially centered on the Au atoms (64%), while the LUMO is essentially centered on the Au (36%) and carbene C atoms (32%), see Figure 6. The band at 252 nm involves a HOMO-2 to LUMO transition, with the HOMO-2 showing a small participation of the Au atoms (16%). TDDFT calculations on the first singlet excited state geometry indicate a single intense band at 344 nm, in good agreement with the experimental emission band at roughly 360 nm, involving the HOMO and the LUMO. The shift of roughly 70 nm of the emission band from the excitation bands at 252 and 277 nm is in reasonable agreement with the experimental shift of the band of **3** from roughly 260 nm in the absorption spectra to roughly 360 nm in the emission spectra. Finally, we also investigated the possibility that the multiplicity of the emitting state is triplet rather than singlet; in this case, a spin-forbidden band is calculated at 402 nm, which results in the rather large deviation of roughly 40 nm from the experimental value. These combined theoretical data, however, do not unequivocally allow the assignment of the multiplicity of the emitting state; this is particularly true considering the dinuclear structure of the complexes, the nature of the metal center, and their mutual interaction.

■ CONCLUSIONS

In conclusion, we have demonstrated that dinuclear dicarbene complexes of gold(I) may display very interesting features such as (i) simple chemical structure, not specifically functionalized
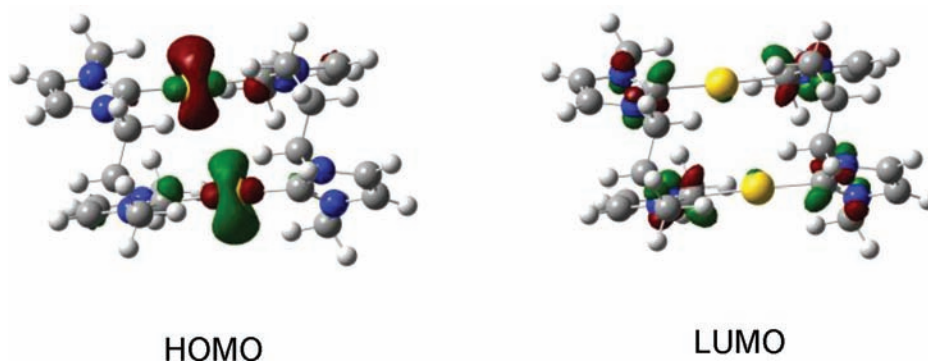

Figure 6. HOMO and LUMO of **3**.

with any chromophore, (ii) almost unitary photoluminescence quantum yield (**3-PF$_6$**, Φ_{em} = 96%) in the solid state, both as a crystal or a powder, (iii) blue emission, that is the less common and thus most technologically valuable color for luminescent materials,[32] and (iv) thermal and photochemical stability. Particularly, the excellent luminescence properties of **3-PF$_6$** in terms of color and intensity make it appealing for electroluminescent devices.[33] It appears that these properties are likely related to the molecular structure of the complex, in particular its short Au⋯Au distance. We are currently working toward the rationalization of these systems and studying the possible color tunability by the introduction of suitable changes in the structure of the carbene ligands.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Absorption spectra of diimizazolium salts, emission spectra of **3-PF$_6$** and **7-PF$_6$** in rigid matrix, coordinates and absolute SCF energies of the DFT and TDDFT optimized geometry of ground state and of the first excited state of **3**, and CIF file for complex **3-PF$_6$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293. (b) "Bioinorganic and Biomedical Chemistry of Gold" special issue: *Coord. Chem. Rev.* **2009**, *253*, 1597.

(2) (a) He, X.; Yam, V. W.-W. *Coord. Chem. Rev.* **2011**, *255*, 2111. (b) Barbieri, A.; Accorsi, G.; Armaroli, N. *Chem. Commun.* **2008**, 2185.

(3) (a) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3. (b) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931.

(4) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412.

(5) (a) Kim, P.-S. G.; Hu, Y.; Brandys, M.-C.; Burchell, T. J.; Puddephatt, R. J.; Sham, T. K. *Inorg. Chem.* **2007**, *46*, 949. (b) Lagunas, M. C.; Mendicute Fierro, C.; Pintado-Alba, A.; de la Riva, H.; Betanzos-Lara, S. *Gold Bull.* **2007**, *40*, 135.

(6) For general references on N-heterocyclic carbene ligands, see: (a) Diez-Gonzalez, S., Ed.; N-Heterocyclic Carbenes: from Laboratory Curiosities to Efficient Synthetic Tools. In *RSC Catalysis Series*; RSC: Cambridge, U.K., 2010. (b) Cazin, C. S. J., Ed.; N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis. In *Catalysis by Metal Complexes*; Springer: Heidelberg, Germany, 2010; Vol. 32. (c) Glorius, F., Ed.; N-Heterocyclic Carbenes in Transition Metal Catalysis. In *Topics in Organometallic Chemistry*; Springer: Heidelberg, Germany, 2007; Vol. 21. (d) Nolan, S. P., Ed.; N-Heterocyclic Carbenes in Synthesis. Wiley-VCH: Weinheim, Germany, 2006.

(7) Muñiz, J.; Wang, C.; Pyykkö, P. *Chem.—Eur. J.* **2011**, *17*, 368.

(8) (a) Carcedo, C.; Knight, J. C.; Pope, S. J. A.; Fallis, I. A.; Dervisi, A. *Organometallics* **2011**, *30*, 2553. (b) Elbjeirami, O.; Rashdan, M. D.; Nesterov, N.; Rawashdeh-Omary, M. A. *Dalton Trans.* **2010**, *39*, 9465.

(c) Jean-Baptiste dit Dominique, F.; Gornitzka, H.; Sournia-Saquet, A.; Hemmert, C. *Dalton Trans.* **2009**, 340. (d) Au, V. K.-M.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2009**, *131*, 9076. (e) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561, and references cited therein. (f) Barnard, P. J.; Wedlock, L. E.; Baker, M. V.; Berners-Price, S. J.; Joyce, D. A.; Skelton, B. W.; Steer, J. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 5966. (g) Wang, H. M. J.; Vasam, C. S.; Tsai, T. Y. R.; Chen, S.-H.; Chang, A. H. H.; Lin, I. J. B. *Organometallics* **2005**, *24*, 486.

(9) Saitoh, M.; Balch, A. L.; Yuasa, J.; Kawai, T. *Inorg. Chem.* **2010**, *49*, 7129.

(10) (a) Rios, D.; Pham, D. M.; Fettinger, J. C.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2008**, *47*, 3442. (b) White-Morris, R. L.; Olmstead, M. M.; Jiang, F.; Balch, A. L. *Inorg. Chem.* **2002**, *41*, 2313. (c) White-Morris, R. L.; Olmstead, M. M.; Jiang, F.; Tinti, D. S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 2327.

(11) (a) Biffis, A.; Gazzola, L.; Tubaro, C.; Basato, M. *ChemSusChem* **2010**, *3*, 834. (b) Buscemi, G.; Basato, M.; Biffis, A.; Gennaro, A.; Isse, A. A.; Natile, M. M.; Tubaro, C. *J. Organomet. Chem.* **2010**, *695*, 2359. (c) Biffis, A.; Gioia Lobbia, G.; Papini, G.; Pellei, M.; Santini, C.; Scattolin, E.; Tubaro, C. *J. Organomet. Chem.* **2008**, *693*, 3760. (d) Biffis, A.; Gazzola, L.; Gobbo, P.; Buscemi, G.; Tubaro, C.; Basato, M. *Eur. J. Org. Chem.* **2009**, 3189. (e) Biffis, A.; Tubaro, C.; Scattolin, E.; Basato, M.; Santini, C.; Papini, G.; Alvarez, E.; Conejero, S. *Dalton Trans.* **2009**, 7223.

(12) Wells, K. D.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Organometallics* **2008**, *27*, 691.

(13) Herrmann, W. A.; Köcher, C.; Gooßen, L. J.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 1627.

(14) Nachtigall, F. M.; Corilo, Y. E.; Cassol, C. C.; Ebeling, G.; Morgon, N. H.; Dupont, J.; Eberlin, M. N. *Angew. Chem., Int. Ed.* **2008**, *47*, 151.

(15) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617–618*, 546.

(16) Okuyama, K.; Sugiyama, J.; Nagahata, R.; Asai, M.; Ueda, M.; Takeuchi, K. *J. Mol. Catal. A: Chem.* **2003**, *203*, 21.

(17) Barnard, P. J.; Baker, M. V.; Berners-Price, S. J.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2004**, 1038.

(18) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1999. *SAINT Software UsersGuide*, Version 6.0; Bruker Analytical X-ray Systems: Madison, WI, 1999. Sheldrick, G. M. *SADABS*; Bruker Analytical X-ray Systems: Madison, WI, 1999. *APEX II Software User Guide*; Bruker AXS Inc., Madison, WI, 2008. *SAINT*, Version 7.06a; Bruker AXS Inc.: Madison, WI, 2008. *SADABS*, Version 2.01; Bruker AXS Inc.: Madison, WI, 2008.

(19) Sheldrick, G. M. *SHELX-97, Programs for Crystal Structure Analysis*, Release 97-2; University of Göttingen: Göttingen, Germany, 1997.

(20) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(21) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(22) De Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

(23) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396. (c) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;

Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(25) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(26) (a) Haeusermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *78*, 1211. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535. (c) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1996**, *105*, 1052.

(27) (a) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327. (b) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

(28) Schwartz, G.; Pfeiffer, M.; Reineke, S.; Walzer, K.; Leo, K. *Adv. Mater.* **2007**, *19*, 3672.

(29) (a) Liu, A.; Zhang, X.; Chen, W.; Qiu, H. *Inorg. Chem. Commun.* **2008**, *11*, 1128. (b) Fränkel, R.; Kniczek, J.; Ponikwar, W.; Nöth, H.; Polborn, K.; Fehlhammer, W. P. *Inorg. Chim. Acta* **2001**, *312*, 235. (c) Wang, W.; Song, H.-B.; Li, Q.-S.; Xu, F.-B.; Zhang, Z.-Z. *Inorg. Chim. Acta* **2005**, *358*, 3653.

(30) (a) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270. (b) Mayer, I. *Int. J. Quantum Chem.* **1984**, *26*, 151.

(31) Guido, C. A.; Jacquemin, D.; Adamo, C.; Mennucci, B. *J. Phys. Chem. A* **2010**, *114*, 13402.

(32) Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 7780.

(33) (a) Gather, M. C.; Köhnen, A.; Meerhlz, K. *Adv. Mater.* **2011**, *23*, 233. (b) Costa, R. D.; Orti, E.; Bolink, H. J.; Graber, S.; Housecroft, C. E.; Constable, E. C. *Adv. Funct. Mater.* **2010**, *20*, 1511.