

Luminescence Quenching of a Novel Phosphorescent Ir(III) Complex/MWCNT Hybrid

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Received December 8, 2011, Accepted January 13, 2012

Key Words : Carbon nanotube, Iridium, Phosphorescence, Donor-acceptor, Photovoltaics

Electron donor-acceptor hybrid systems have received great interest in photovoltaic applications,¹⁻⁵ in which photo-induced electrons of photosensitizers convert to electrical energy *via* electron transfer to electron acceptors. The electron transfer efficiency is determined by the competition between recombination of the excited electrons to the ground state and electron transfer of the excited electrons to acceptors. Consequently, the photosensitizer with a slow rate of recombination, which means a long lifetime for the excited electrons, could be a good candidate for achieving high electron transfer efficiency in donor-acceptor hybrids. Phosphorescence, emissive decay of the excited electrons to the ground state through intersystem crossing between singlet and triplet states by a strong spin-orbit coupling, shows a longer lifetime for the excited electrons than fluorescence, emissive decay between singlet states.⁶ Here, we present the synthesis of a novel Ir-based phosphorescent complex and demonstrate its excellent luminescence quenching when it forms a hybrid complex with multiwall carbon nanotubes (MWCNTs). The system shows an almost 100% quenching efficiency of the excited electrons. To the best of our knowledge, this is the first investigation of a Ir-based phosphorescent photosensitizer for possible photovoltaic applications.

Carbon nanotubes (CNTs) composed of an extended π -electron system with one dimensional structure have been used for photovoltaic applications as an electron acceptor of donor-acceptor hybrid systems because of their high electron mobility. CNTs have often showed excellent electron transfer efficiency in hybrid systems containing fluorescent photosensitizers, such as porphyrins, pyrenes, polymers, and organometallic compounds.^{7,8} Consequently, we thought that hybrid systems of the phosphorescent d^6 Ir(III) complex with a long lifetime⁷ and CNTs could show excellent performance for photovoltaic applications.

In the CNT-based hybrid systems, the systems containing covalently tethered photosensitizers on CNTs have frequently showed good performances, such as good stability and high electron transfer efficiency.⁹ Thus, we designed a novel tris-cyclometalated iridium(III) complex $[\text{Ir}(\text{ppy})_2(\text{hppy})]$ (**1**), bis(2-phenylpyridyl)-4-(4'-hydroxyphenyl)-2-phenylpyridyliridium(III), that has one -OH end group and synthesized by heating dichloro-bridged dimer $[(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2(\text{ppy})_2]$ with two-fold amount of 4-hydroxyphenyl-2-

phenylpyridine (hppy) (see the experimental section and supporting information (SI)). Such -OH group is useful for covalent attachment of the Ir complex on -COOH groups of functionalized MWCNTs *via* esterification (Figure 1). Complex **1** showed a long excited-state lifetime (500 ± 6 ns) studied by time-resolved measurement when it was excited at 450 nm, confirming that it is a phosphorescent complex (inset in Figure 2(b)).^{7,10} On the other hand, fluorescent materials usually have a shorter lifetime, below several tens of nanoseconds.⁶

Carboxyl acid groups on the MWCNTs were activated by reaction with SOCl_2 and then mixed with complex **1** in toluene containing triethylamine with reflux for 1 day, resulting in Ir complex/MWCNT hybrids ($[\text{Ir}(\text{ppy})_2(\text{hppy})]_n\text{-g-MWCNTs}$, **2**) *via* covalent attachment. The esterification between carboxyl and hydroxyl groups is well known to generate covalent bonding. The products were filtered through a membrane filter (0.1 μm pore size), and the residual complex **1** was thoroughly removed by washing with dichloromethane and tetrahydrofuran 5 times each and then dried in a vacuum. The resulting product was obtained as black powder.

The UV-vis absorption spectrum (Figure 2(a)) of the ethanol solution of the complex **1** shows a strong band at 280 nm corresponding to the ligand-centered (LC) transition, that is, a spin-allowed ($\pi\text{-}\pi^*$) transition of the phenylpyridyl

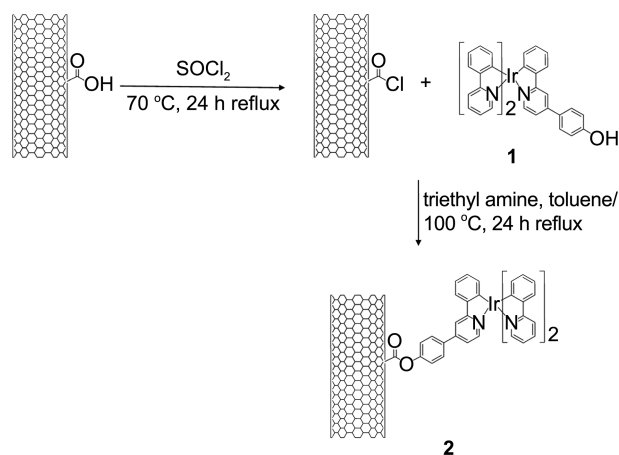


Figure 1. Schematic diagram for preparation of the hybrid $[\text{Ir}(\text{ppy})_2(\text{hppy})]_n\text{-g-MWCNTs}$ (**2**).

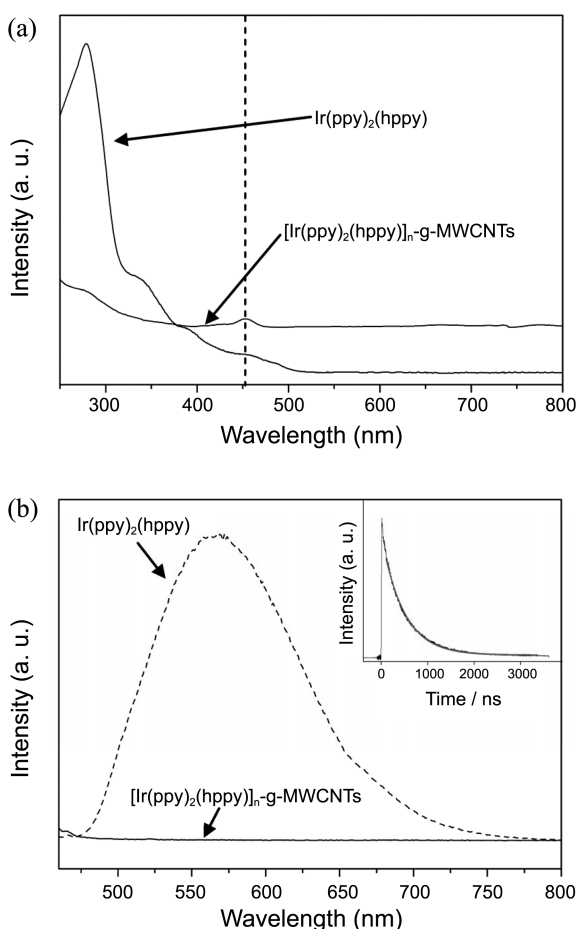


Figure 2. (a) UV-vis absorption and (b) emission spectra of **1** and **2**. Inset in (b): time-resolved emission decay of **1** (450 nm excitation) at room temperature in oxygen-free chloroform.

ligand.¹¹⁻¹³ The lower energy bands in the region from 320 nm to 520 nm could be assigned to both ³LC and allowed/spin-forbidden metal ligand charge transfer (MLCT) transitions.¹¹⁻¹³ Importantly, the lowest absorption band at around 450 nm corresponds to the spin-forbidden MLCT band, which is facilitated by strong spin-orbit coupling of the Ir(III) center.^{7,8} The absorption spectrum of the suspension of the hybrid **2** in ethanol shows intense bands appearing at 280 nm and 450 nm, which are attributed to the characteristic absorption of the core unit of the complex **1**, supporting successful attachment of the complex **1** on the MWCNTs.

To elucidate the quenching efficiency of the excited electrons in the hybrid system, the emission spectra (Figure 2(b)) of both the complex **1** and the hybrid **2** were measured in chloroform separately when they were excited at 430, 450, or 500 nm. Upon excitation at 450 nm, a photoluminescence (PL) spectrum of the complex **1** in solution shows a strong emission band at 569 nm. On the other hand, that of the suspension of hybrid **2** exhibits no emission, meaning that the excited electrons of the Ir complex were quenched without recombination to the ground state (almost 100% quenching efficiency). The excellent PL quenching efficiency in the hybrid **2** could be ascribed to the long excited-

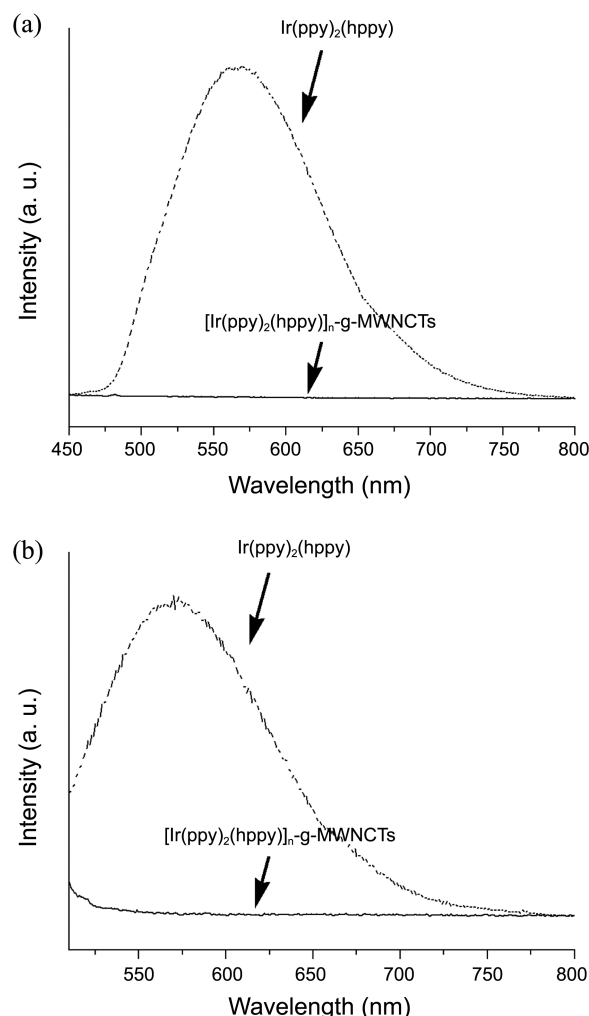


Figure 3. PL spectra of **1** (dashed line) and **2** (solid line) in chloroform excited at (a) 430 nm and (b) 500 nm.

state lifetime (500 ± 6 ns) of the phosphorescent Ir complex. Such a long lifetime of the excited electrons could support a high possibility for electron transfer to the MWCNTs before recombination to the ground state. In other excitation wavelengths (430 nm, 500 nm), the hybrid system also showed an excellent quenching efficiency (Figure 3).

Attachment of the complex **1** on the MWCNTs in hybrid **2** was further investigated by Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and energy dispersive X-ray spectroscopy (EDS). The FT-IR spectrum of hybrid **2** showed specific peaks corresponding to complex **1**, which were not observed in that of MWCNT-COOH, confirming successful attachment of the Ir complex (see SI for details). The XPS data also confirmed the successful attachment of complex **1** on the MWCNTs. After the grafting step, new peaks corresponding to N and Ir atoms in the complex **1** were observed in the XPS spectrum of hybrid **2** separately (see SI). The number of Ir atoms in the hybrid **2** was found to be about 3.5% relative to C atoms, based on calculation of the peak areas in the XPS spectrum. The EDS spectrum of hybrid **2** clearly showed an iridium peak that was not shown in that of MWCNT-COOH, sup-

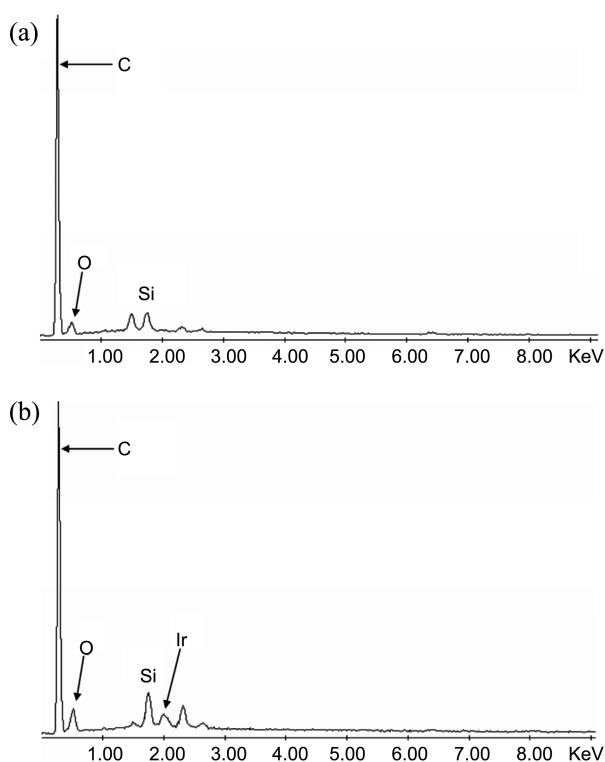


Figure 4. EDS data for (a) MWCNTs-COOH, (b) $[\text{Ir}(\text{ppy})_2(\text{hppy})]_n\text{-g-MWCNTs, 2}$.

porting the existence of complex **1** in the hybrid after attachment (Figure 4).

To summarize, we describe the synthesis of a novel phosphorescent Ir(III) complex, bis(2-phenylpyridyl)-4-(4'-hydroxyphenyl)-2-phenylpyridyliridium (III) $[\text{Ir}(\text{ppy})_2(\text{hppy})]$ (**1**) and a hybrid system (**2**) composed of the Ir(III) complex and MWCNTs, which are covalently linked. The phosphorescent complex **1** has long lifetime (500 ± 6 ns) in the excited state. We found that the hybrid system shows a luminescence quenching efficiency of almost 100%. Although the detailed mechanism of the quenching was not fully revealed, we think that the long lifetime of the excited electrons of the iridium complex could result in a high possibility for electron transfer to the MWCNTs, and in turn, also result in the excellent quenching efficiency. Using a phosphorescent photosensitizer with a long lifetime could be an important step to develop donor-acceptor hybrid systems for photovoltaic applications.

Experimental Section

General Consideration. The experiments were carried out in an inert nitrogen atmosphere using standard Schlenk techniques. Toluene, *n*-hexane, and tetrahydrofuran (THF) were distilled from a Na-K alloy, diethyl ether from *N*-benzophenone ketyl. All reagents were used without any further purification after purchasing them from Sigma-Aldrich (4-methoxyphenylboronic acid, thionyl chloride, and triethylamine), and Strem (iridium chloride hydrate). 4-Bromo-2-phenylpyridine,¹⁴ tetrakis(2-phenylpyridine- C^2, N^1)

(μ -dichloro)diiridium,¹⁵ and COOH functionalized MWCNTs (MWCNTs-COOH)¹⁶ were prepared following the procedures in the literature. CDCl_3 from Cambridge Isotope Laboratories was used after drying over activated molecular sieves (5 Å).

Instruments. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ^1H , 100.62 MHz for ^{13}C) at ambient temperature. Chemical shifts are given in ppm and are referenced against external Me_4Si (^1H , ^{13}C). The Fourier Transformed infrared (FT-IR) spectrum was obtained using a Bruker Equinox-55 FT-IR spectrophotometer. Elemental analyses were performed on an EA1110 (FISONS Instruments) at KAIST. X-ray photoelectron spectroscopy (XPS) measurement was performed using a VG-Scientific ESCALAB 250 spectrometer (UK) with a monochromatized Al K α X-ray source. Emitted photoelectrons were detected using a multichannel detector at a take-off angle of 90° relative to the surface. During the measurements, the base pressure was $1.33_{10}7\text{--}1.33_{10}8$ Pa. Survey spectra were obtained at a resolution of 1 eV from three scans, and high-resolution spectra were acquired at a resolution of 0.05 eV from 5-20 scans. UV-vis and emission spectra were recorded on a Jasco V-530 and a Spex Fluorog-3 Luminescence spectrophotometer in ethanol with a 1-cm quartz cuvette at ambient temperature, respectively. The detailed conditions are given in the figure captions. Time-resolved measurements were made with a tunable laser pulse (~ 10 $\mu\text{J}/\text{pulse}$, $\Delta t \sim 6$ ns) output from a dye laser (Lambda Physik, Scanmate 2) pumped by the third harmonic output of a Nd:YAG laser (Continuum, Precision II).

Syntheses.

4-Hydroxyphenyl-2-phenylpyridine (hppy): The toluene solution of 4-bromo-2-phenylpyridine (2.14 g, 9.13 mmol), 2.0 M aqueous solution of Na_2CO_3 (9.13 mL), and 4-methoxyphenylboronic acid (1.53 g, 10.04 mmol) dissolved in ethanol were added in turn to a 50 mL toluene solution of $\text{Pd}(\text{PPh}_3)_4$ (3 mol %, 0.31 g, pph: phenylpyridine). The reaction mixture was refluxed for 12 h. After cooling to room temperature and adding water, the organic phase was extracted with ethyl acetate and washed with purified H_2O and aqueous NaCl solution 3 times. The obtained solution was dried over MgSO_4 and evaporated. Purification of the crude product by column chromatography (hexane/ethyl acetate = 4) produced 4-methoxyphenyl-2-phenylpyridine as white solid. The product (2.05 g, 7.88 mmol) was dissolved in 20 mL of concentrated hydrochloric acid. The reaction mixture was kept at 130°C for 24 h. After cooling to room temperature and adding an aqueous solution of NaHCO_3 , the organic phase was extracted with ethyl acetate and washed with NaCl (aq). The obtained solution was dried over MgSO_4 and evaporated to yield the white solid. The resulting white solid was filtered off and washed with dichloromethane (yield: 67%).

^1H NMR (MEOD, 400.13 MHz, ppm) δ 8.55 (t, 1H), 7.94-7.98 (m, 3H), 7.68 (t, 2H), 7.57 (t, 1H), 7.44-7.49 (m, 3H), 6.92 (t, 2H).

^{13}C NMR (MEOD, 400.13 MHz, ppm) δ 160.32, 159.57, 151.32, 150.52, 140.73, 130.18, 130.00, 129.85, 129.47, 128.32, 120.77, 119.64, 117.07.

Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_1\text{O}_1$: C 82.55, H 5.30, N 5.66. Found: C 81.81, H 5.38, N 5.61.

Ir(ppy)₂(hppy) (1): The 2.0 M aqueous solution of Na_2CO_3 (3.73 mL) and 4-hydroxyphenyl-2-phenylpyridine (0.92 g, 3.73 mmol) in 2-methoxyethanol was added slowly to the solution (30 mL) of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (2.0 g, 1.86 mmol) in 2-methoxyethanol. The reaction mixture was refluxed for 24 h to give a deep yellow solution. After the mixture was cooled to room temperature, distilled water was added, and the resulting solid was filtered off, washed with distilled water, and air-dried. The crude product was dissolved with dichloromethane and purified by column chromatography (hexane/ethyl acetate = 1) to yield the yellow solid (yield: 0.77 g, 55.2%).

^1H NMR (CDCl_3 , 400.13 MHz, ppm) δ 8.68 (d, 1H), 8.13 (d, 1H), 8.06 (s, 1H), 8.04 (d, 1H), 7.86 (d, 1H), 7.78 (d, 2H), 7.67 (m, 2H), 7.56-7.60 (m, 1H), 7.54 (d, 2H), 7.35-7.50 (m, 3H), 7.05 (d, 1H), 6.90-6.96 (m, 5H), 6.75-6.80 (m, 2H), 6.71 (t, 2H), 6.60-6.68 (m, 1H), 6.47 (d, 1H), 5.12 (s, 1H).

^{13}C NMR (CDCl_3 , 400.13 MHz, ppm) δ 117.78, 175.32, 170.52, 168.53, 167.87, 159.73, 157.13, 153.21, 151.18, 148.06, 147.87, 145.40, 144.79, 142.31, 138.03, 135.44, 133.94, 132.77, 130.56, 129.95, 129.90, 129.88, 129.52, 128.82, 128.45, 128.39, 127.18, 124.06, 123.90, 121.98, 121.20, 121.15, 120.79, 119.82, 118.74, 118.53, 118.30, 116.09, 116.00.

Anal. Calcd for $\text{C}_{39}\text{H}_{28}\text{N}_3\text{O}_1\text{Ir}$: C 62.72, H 3.78, N 5.63. Found: C 62.95, H 3.87, N 5.60.

ESI-MS: m/z calcd 747.2. found 748.7.

$[\text{Ir}(\text{ppy})_2(\text{hppy})]_n\text{-g-MWCNTs (2):}$ A slurry of MWCNTs-COOH (45 mg) in 45 mL of thionyl chloride was refluxed at 70 °C for 24 h. After cooling to room temperature, the thionyl chloride was decanted. The MWCNTs-COCl was washed with excess THF and dried at 70 °C overnight in a vacuum. A mixture of MWCNTs-COCl, $\text{Ir}(\text{ppy})_2(\text{hppy})$ (50 mg, 0.067 mmol) and triethylamine (0.2 mL) in toluene was refluxed. After 24 h, the toluene was decanted and the mixture was washed with excess THF several times. The

resulting product was filtered through a membrane filter (0.1 μm pore size), and the residual $\text{Ir}(\text{ppy})_2(\text{hppy})$ was removed by washing with dichloromethane and THF and then dried in a vacuum.

Acknowledgments. S. Park appreciates support from INHA University Research Grant (INHA-44083).

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