Synthesis, Characterization, and Second-Harmonic Generation Studies of Rhenium(I) Surfactant Complexes in Langmuir−Blodgett Films

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A series of rhenium(I) surfactant complexes of general formula *fac*-[Re(CO)$_3$(bpy)(L)]PF$_6$ (bpy = 2,2′-bipyridine, L = 4-(4′-octadecyloxyphenylazo)pyridine (L1), 4-(4′-octadecyloxyphenylstilbazole)pyridine (L2), 4-(4′-octadecyloxyphenylethynyl)pyridine (L3)) were synthesized and characterized, and their photophysical and photochemical properties studied. The X-ray crystal structure of the complex *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ has been determined. The formation and optical properties of these complexes in Langmuir−Blodgett (LB) films were studied by surface pressure−area (π−A) isotherms and UV−visible and luminescence spectroscopy. Their second-harmonic generation (SHG) behavior has also been investigated. These Re(I) surfactant complexes were shown to exhibit first-order hyperpolarizabilities comparable to, and in some cases slightly higher than, those of their organic analogues.

Introduction

Nonlinear optical (NLO) materials are currently under intensive investigation for their potential application in optical signal processing and telecommunications.[1] Much effort has been placed on the design and syntheses of molecules with large nonlinearities and on assembling and fabricating the molecules into microscopic structures such as crystals,[2] Langmuir−Blodgett (LB) films,[3] self-assembly films,[4] and poled polymers.[5] It is well-known that significant second-harmonic generation (SHG) can only occur in noncentrosymmetric media for dipolar molecules. The Langmuir−Blodgett (LB) technique, which is one of the powerful tools of making highly homogeneous, ordered ultrathin films, has been exploited to build materials with a non-centrosymmetric packing arrangement.[6] A number of π-conjugated organic compounds with electron-donating and -accepting groups have been known to show SHG behavior when incorporated into LB films.[3]

A number of organometallic compounds have also been shown to exhibit second-order NLO properties since their reports appeared in the late 1980s.[7] Large NLO responses are usually observed in organometallic molecules that possess large charge-transfer character.[8] Recent work by us has shown that the rhenium(I) diimine tricarbonyl complexes, which are well-known for the rich photophysical and photochemical properties of their MLCT excited states,[9,10] show, in addition to their chemosensory[11] and optical switching properties,[10b] interesting NLO responses.[10i,j,12]

In this report, the synthesis and characterization of a series of rhenium(I) surfactant complexes with extended donor−acceptor pyridine ligands, *fac*-[Re(CO)$_3$(bpy)(L)]PF$_6$ (bpy = 2,2′-bipyridine, L = 4-(4′-octadecyloxyphenylazo)pyridine (L1), 4-(4′-octadecyloxyphenylstilbazole)pyridine (L2), 4-(4′-octadecyloxyphenylethynyl)pyridine (L3)), are described. The formation and

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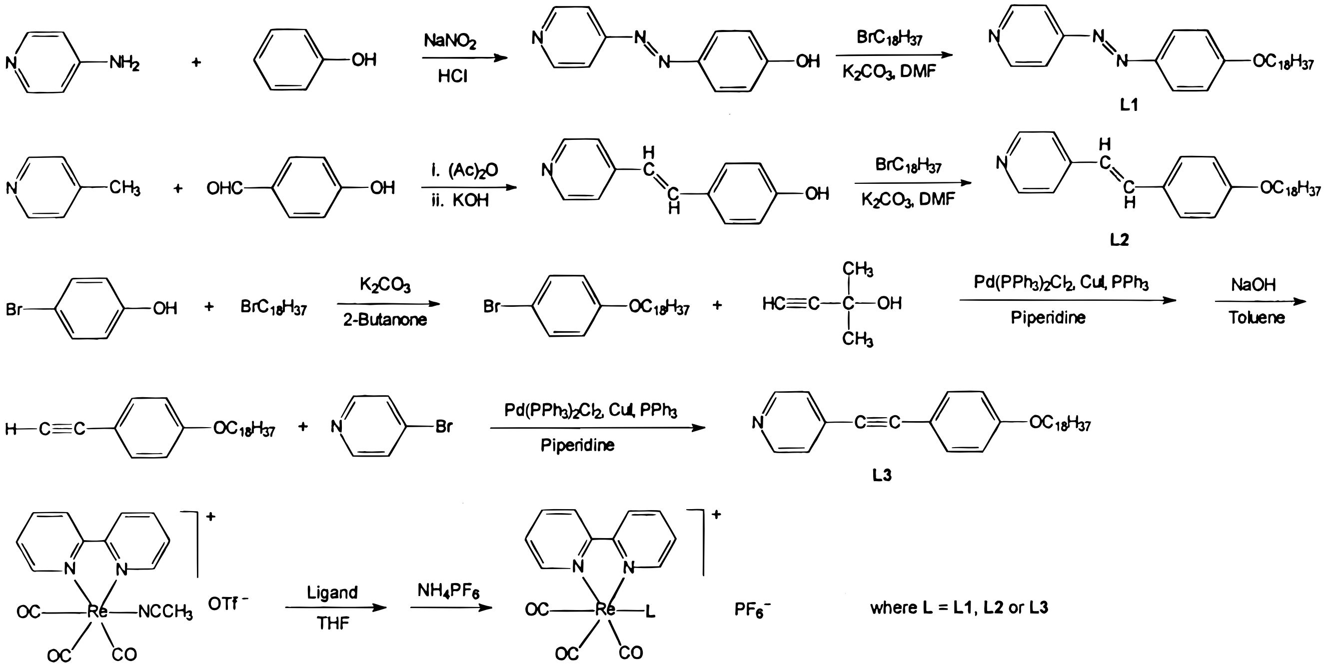
Scheme 1



optical properties of these complexes in LB films have been studied by surface pressure−area (π−A) isotherms and UV−visible and luminescence spectroscopy. The SHG capabilities of these complexes have also been assessed.

Experimental Section

Materials. $Re(CO)_5Cl$ (98%, Strem), 2,2′-bipyridine (99%, Lancaster), silver trifluoromethanesulfonate (99%, Aldrich), and ammonium hexafluorophosphate (99.5%, Strem) were used as received. 2-Methyl-3-butyn-2-ol (98%, Acros) was distilled before use. Piperidine (99%, Acros) was distilled over CaH_2. All other solvents for synthesis were of analytical grade and were used without further purification.

Synthesis. Synthetic schemes for the ligands and the rhenium(I) complexes are summarized in Scheme 1.

Synthesis of Pyridyl Ligands. *trans*-4-(4′-Hydroxyphenylazo)pyridine,[13] 4-octadecyloxyphenylacetylene,[14] and ligand L2[15] were prepared according to literature procedures.

***trans*-4-(4′-Octadecyloxyphenylazo)pyridine (L1).** Unlike the synthesis of *trans*-4(4′-methoxyphenylazo)pyridine analogue,[13] L1 was synthesized by stirring a mixture of *trans*-4-(4′-hydroxyphenylazo)pyridine (0.5 g, 2.5 mmol), 1-bromooctadecane (0.8 g, 2.4 mmol), and potassium carbonate (0.69 g, 5 mmol) in dimethylformamide (DMF) (15 mL) at room temperature for 3 days. Potassium bromide produced was filtered off, and the DMF was removed by distillation under reduced pressure. The residue was redissolved in chloroform (15 mL) and washed with water (3 × 15 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. Filtration and subsequent removal of the solvent by rotary evaporation of the organic layer yielded the crude products, which were purified by column chromatography on silica gel using chloroform as eluent to afford 0.61 g of the pale yellow desired product. Yield: 56%. ^1H NMR (300 MHz, $CDCl_3$, relative to Me_4Si): δ 8.77 (d, 2H, $J = 6.1$ Hz, pyridyl), 7.95 (d, 2H, $J = 9.0$ Hz, phenyl), 7.67 (d, 2H, $J = 6.2$ Hz, pyridyl), 7.02 (d, 2H, $J = 9.0$ Hz, phenyl), 4.06 (t, 2H, $J = 6.6$ Hz, $-OCH_2-$), 1.83 (m, 2H, $-CH_2-$), 1.48 (m, 2H, $-CH_2-$), 1.26 (m, 28H, $-CH_2-$), 0.88 (t, 3H, $J = 6.4$ Hz, $-CH_3$). Anal. Found: C, 76.36; H, 10.04; N, 9.48. Calcd for $C_{29}H_{45}N_3O\cdot 1/4H_2O$: C, 76.35; H, 9.94; N, 9.21.

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4-(4′-Octadecyloxyphenylethynyl)pyridine (L3). L3 was synthesized by modification of a literature method for 5,5′-[(4-hexadecyloxyphenyl)ethynyl]-2,2′-bipyridine.[16] A mixture of 4-bromopyridine hydrochloride (0.21 g, 1.1 mmol) and 4-octadecyloxyphenylacetylene (0.37 g, 1 mmol) was dissolved in freshly distilled piperidine (10 mL). Copper(I) iodide (10 mg), dichlorobis(triphenylphosphine)palladium(II) (10 mg), and triphenylphosphine (40 mg) were added as the catalysts. The mixture was heated to reflux under nitrogen for 24 h. The purification was the same as that of L1 except that *n*-hexanes−ethyl acetate (3:1, v/v) was used as eluent instead of chloroform. Recrystallization from ethyl acetate yielded 0.34 g of the pure product. Yield: 75%. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, ppm relative to $\mathrm{Me_4Si}$): δ 8.58 (dd, 2H, $J_1 = 4.5$ Hz, $J_2 = 1.6$ Hz, pyridyl), 7.48 (d, 2H, $J = 8.8$ Hz, phenyl), 7.35 (dd, 2H, $J_1 = 4.5$ Hz, $J_2 = 1.6$ Hz, pyridyl), 6.89 (d, 2H, $J = 8.8$ Hz, phenyl), 3.98 (t, 2H, $J = 6.6$ Hz, $-\mathrm{OCH_2}-$), 1.79 (m, 2H, $-\mathrm{CH_2}-$), 1.46 (m, 2H, $-\mathrm{CH_2}-$), 1.26 (m, 28H, $-(\mathrm{CH_2})_{14}-$), 0.88 (t, 3H, $J = 6.3$ Hz, $-\mathrm{CH_3}$). ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, ppm relative to $\mathrm{Me_4Si}$): 159.96, 149.68, 133.43, 131.86, 125.36, 114.64, 113.81 (pyridyl and phenyl C), 94.45, 85.57 ($-\mathrm{C{\equiv}C}-$), 68.11, ($-\mathrm{OCH_2}-$), 31.94, 29.72, 29.61, 29.39, 29.16, 26.01, 22.71, 14.13 (alkyl C). EI-MS *m*/*z*: 447 ($\mathrm{M^+}$). Anal. Found: C, 83.33; H, 10.37; N, 3.10. Calcd for $\mathrm{C_{31}H_{45}N_3O}$: C, 83.17; H, 10.13; N, 3.13.

Synthesis of Rhenium(I) Complexes. The rhenium(I) complexes *fac*-$[\mathrm{Re(CO)_3(bpy)Cl}]$[9d,j,10] and *fac*-$[\mathrm{Re(CO)_3(bpy)(MeCN)}]$OTf [10,17] were prepared according to literature methods.

General Synthesis of *fac*-$[\mathbf{Re(CO)_3(bpy)(L)}]\mathbf{PF_6}$. This was synthesized by modification of a reported procedure.[17] A mixture of *fac*-$[\mathrm{Re(CO)_3(bpy)(MeCN)}]$OTf (1 equiv) and ligand L (1.5 equiv) in tetrahydrofuran (THF) was heated to reflux under nitrogen for 12 h. The resulting solution was allowed to cool and evaporated to dryness under vacuum. The residue was then dissolved in methanol and metathesized to its $\mathrm{PF_6^-}$ salt upon addition of a saturated methanolic solution of $\mathrm{NH_4PF_6}$. The solid obtained was recrystallized by vapor diffusion of diethyl ether into a dichloromethane solution of the product.

***fac*-$[\mathbf{Re(CO)_3(bpy)(L1)}]\mathbf{PF_6}$:** red crystalline solid, yield 85%. Mp: 120.5 °C. ^{1}H NMR (300 MHz, acetone-d_6, ppm relative to $\mathrm{Me_4Si}$): δ 9.53 (d, 2H, $J = 5.6$ Hz, 6,6′-H of bpy), 8.75 (m, 4H, 3,3′-H of bpy and pyridyl H *ortho* to N), 8.50 (m, 2H, 4,4′-H of bpy), 8.04 (m, 2H, 5,5′-H of bpy), 7.94 (d, 2H, $J = 9.0$ Hz, phenyl H of L1), 7.72 (d, 2H, $J = 6.8$ Hz, pyridyl H *meta* to N), 7.15 (d, 2H, $J = 9.1$ Hz, phenyl H of L1), 4.15 (t, 2H, $J = 6.5$ Hz, $-\mathrm{OCH_2}-$), 1.82 (m, 2H, $-\mathrm{CH_2}-$), 1.49 (m, 2H, $-\mathrm{CH_2}-$), 1.28 (m, 28H,$-(\mathrm{CH_2})_{14}-$), 0.87 (t, 3H, $J = 6.4$ Hz, $-\mathrm{CH_3}$). UV−vis ($\mathrm{CH_2Cl_2}$, λ/nm ($\epsilon \times 10^{-4}$/dm^{3}mol^{-1}cm^{-1})): 396 (3.36). UV−vis (LB film, λ/nm): 388. IR (Nujol, ν/cm^{-1}): 2031 (s) ν(CO), 1936 (s) ν(CO), 1915 (s) ν(CO). Positive FAB-MS *m*/*z*: 879 $\{\mathrm{M}\}^+$, 427 $\{\mathrm{M} - \mathrm{L1}\}^+$. Anal. Found: C, 49.26; H, 5.13; N, 6.91. Calcd for *fac*-$[\mathrm{Re(CO)_3(bpy)L1}]\mathrm{PF_6}$: C, 49.27; H, 5.18; N, 6.84.

***fac*-$[\mathbf{Re(CO)_3(bpy)(L2)}]\mathbf{PF_6}$:** yellow crystalline solid, yield 84%. Mp: 142 °C. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, ppm relative to $\mathrm{Me_4Si}$): δ 9.07 (d, 2H, $J = 5.4$ Hz, 6,6′-H of bpy), 8.54 (d, 2H, $J = 8.2$ Hz, 3,3′-H of bpy), 8.27 (d, 2H, $J = 7.9$ Hz, 4,4′-H of bpy), 7.95 (d, 2H, $J = 6.7$ Hz, pyridyl H *ortho* to N), 7.73 (m, 2H, 5,5′-H of bpy), 7.41 (d, 2H, $J = 8.8$ Hz, phenyl H of L2), 7.31 (d, 2H, $J = 6.7$ Hz, pyridyl H *meta* to N), 7.25 (d, 1H, $J = 16$ Hz, vinyl H of L2), 6.85 (d, 2H, $J = 8.8$ Hz, phenyl H of L2), 6.70 (d, 1H, $J = 16$ Hz, vinyl H of L2), 3.95 (t, 2H, $J = 6.5$ Hz, $-\mathrm{OCH_2}-$), 1.77 (m, 2H, $-\mathrm{CH_2}-$), 1.43 (m, 2H, $-\mathrm{CH_2}-$), 1.25 (m, 28H, $-(\mathrm{CH_2})_{14}-$), 0.87 (t, 3H, $J = 6.4$ Hz, $-\mathrm{CH_3}$). UV−vis ($\mathrm{CH_2Cl_2}$, λ/nm ($\epsilon \times 10^{-4}$/dm^{3}mol^{-1}cm^{-1})): 370 (2.92). UV−vis (LB film, λ/nm): 366. IR (Nujol, ν/cm^{-1}): 2028 (s) ν(CO), 1929 (s) ν(CO), 1919 (s) ν(CO). Positive FAB-MS *m*/*z*: 877 $\{\mathrm{M}\}^+$, 427 $\{\mathrm{M} - \mathrm{L2}\}^+$. Anal. Found: C, 51.50; H, 5.35; N, 3.83. Calcd for *fac*-$[\mathrm{Re(CO)_3(bpy)L2}]\mathrm{PF_6}$: C, 51.76; H, 5.39; N, 4.12.

***fac*-$[\mathbf{Re(CO)_3(bpy)(L3)}]\mathbf{PF_6}$:** yellow-orange crystalline solid, yield 75%. Mp: 136.5 °C. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, ppm relative to $\mathrm{Me_4Si}$): δ 9.07 (d, 2H, $J = 5.0$ Hz, 6,6′-H of bpy), 8.56 (d, 2H, $J = 8.2$ Hz, 3,3′-H of bpy), 8.29 (m, 2H, 4,4′-H of bpy), 8.05 (d, 2H, $J = 6.1$ Hz, pyridyl H *ortho* to N), 7.75 (m, 2H, 5,5′-H of bpy), 7.41 (d, 2H, $J = 8.8$ Hz, phenyl H of L3), 7.32 (d, 2H, $J = 6.1$ Hz, pyridyl H *meta* to N), 6.85 (d, 2H, $J = 8.8$ Hz, phenyl H of L3), 3.95 (t, 2H, $J = 6.5$ Hz, $-\mathrm{OCH_2}$-), 1.77 (m, 2H, $-\mathrm{CH_2}-$), 1.43 (m, 2H, $-\mathrm{CH_2}-$), 1.25 (m, 28H, $-(\mathrm{CH_2})_{14}-$), 0.87 (t, 3H, $J = 6.3$ Hz, $-\mathrm{CH_3}$). UV−vis ($\mathrm{CH_2Cl_2}$, λ/nm ($\epsilon \times 10^{-4}$/dm^{3}mol^{-1}cm^{-1})): 366 (3.47). UV−vis (LB film, λ/nm): 350. IR (Nujol, ν/cm^{-1}): 2035 (s) ν(CO), 1942 (s) ν(CO), 1908 (s) ν(CO), 2185(v), 2219 (m) ν(C≡C). Positive FAB-MS *m*/*z*: 874 $\{\mathrm{M}\}^+$, 427 $\{\mathrm{M} - \mathrm{L3}\}^+$. Anal. Found: C, 51.77; H, 5.12; N, 3.78. Calcd for *fac*-$[\mathrm{Re(CO)_3(bpy)L3}]\mathrm{PF_6}$: C, 51.87; H, 5.21; N, 4.13.

Physical Measurements and Instrumentation. The UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as Nujol mulls on a Bio-Rad FTS-7 spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog-2 111 spectrofluorometer with or without Corning filters. Low-temperature (77 K) spectra were recorded using an optical Dewar sample holder. Proton NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer with chemical shifts reported relative to tetramethylsilane ($\mathrm{Me_4Si}$). Positive ion fast-atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry in Beijing, Chinese Academy of Sciences.

Emission lifetime measurements were made using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals were recorded on a Tektronix TDS 620A digital oscilloscope and analyzed using a program for exponential fits according to the equation $I(t) = I_0 \exp(-t/\tau)$, where $I(t)$ stands for emission intensity at time t after the laser pulse and I_0 is the initial intensity at $t = 0$. All solutions for photophysical studies were prepared under vacuum in a 10 cm^3 round-bottom flask equipped with a sidearm 1 cm fluorescence cuvette sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze−pump−thaw cycles.

Langmuir−Blodgett (LB) Film Preparation. Ultrapure water (resistivity >18 MΩ cm) was obtained from an Elga UHQ PS apparatus and was immediately used for the Z-type LB film preparation. The quartz substrates were made hydrophilic by consecutive sonication in detergent for 30 min and acetone for 15 min and soaking in both chromic acid and piranha solution (30% $\mathrm{H_2O_2{-}H_2SO_4}$, 3:7 v/v) for 8 h each before they were finally washed repeatedly with copious amounts of distilled and ultrapure water. The complexes in dichloromethane (1.02 mg cm^{-3} for *fac*-$[\mathrm{ReCO)_3(bpy)(L1)}]\mathrm{PF_6}$, 1.04 mg cm^{-3} for *fac*-$[\mathrm{Re(CO)_3(bpy)(L2)}]\mathrm{PF_6}$, and 1.00 mg cm^{-3} for *fac*-$[\mathrm{Re(CO)_3(bpy)(L3)}]\mathrm{PF_6}$) were spread onto a pure water phase (pH 5.4, 18 °C) in a Nima model-622 computer-controlled trough. After a 15 min period to allow for the evaporation of the solvent, surface pressure−area ($\pi - A$) isotherms were recorded at a barrier compression speed of 150 cm^2 min^{-1}. The monolayers formed under a constant surface pressure (30 mN m^{-1} for *fac*-$[\mathrm{Re(L1)(CO)_3(bpy)}]\mathrm{PF_6}$, 25 mN m^{-1} for both *fac*-$[\mathrm{Re(L2)(CO)_3(bpy)}]\mathrm{PF_6}$, and *fac*-$[\mathrm{Re(L3)(CO)_3(bpy)}]\mathrm{PF_6}$) were transferred onto hydrophilically treated quartz substrates after maintaining the pressure constant at the transfer pressure for 15 min for stabilization, at a dipping speed of 5 mm min^{-1}. The transfer ratios were close to unity.

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(16) El-Ghayoury, A.; Douce, L.; Ziessel, R. *Liq. Cryst.* **1996**, *21*, 143.

(17) (a) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commum.* **1984**, 1244. (b) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885.

Table 1. Crystal and Structure Determination Data for *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$

formula	[$C_{42}H_{53}N_5O_4Re$]$^+$PF$_6^-$
fw	1023.08
T, K	301
a, Å	9.275(2)
b, Å	20.345(3)
c, Å	24.350(3)
α, deg	83.52(2)
β, deg	87.61(2)
γ, deg	80.49(2)
V, Å^3	4501(1)
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
Z	4
F(000)	2064
D_{calcd}, g cm^{-3}	1.509
cryst dimens, mm	0.40 × 0.25 × 0.05
λ, Å (graphite monochromated, Mo Kα)	0.71073
μ(Mo Kα), cm^{-1}	28.06
collection range	$2\theta_{\max} = 51.2°$ (h, 0 to 11; k, −23 to 24; l, −29 to 29)
oscillation, deg	3
no. of images collected	70
distance, mm	120
exposure time, s	400
no. of data collected	35946
no. of unique data	14530
R_{int}	0.037
no. of data used in refinement, m	10251 ($I > 3\sigma(I)$)
no. of params refined, p	1011
$R(F_o)^a$	0.038
$R_w(F_o)^a$	0.054
goodness-of-fit, S	1.77
maximum shift, (shift/error)$_{\max}$	0.04 (for atoms of the complex cations)
residual extrema in final diff map, e Å^{-3}	+1.04, −1.03

[a] $w = 4F_o^2/\sigma^2(F_o)^2$, where $\sigma^2(F_o)^2 = [\sigma^2(I) + (0.035F_o^2)^2]$ with $I > 3\sigma(I)$.

Second-Harmonic Generation (SHG) Measurements. The setup for SHG measurements was similar to that reported in the literature.[18] The source was the fundamental 1064 nm output of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. The 532 nm signals generated were recorded on a Tektronix TDS-620A digital oscilloscope. SHG measurements were performed in the transmission mode with the fundamental beam at 45° to the monolayer film. Prior to each measurement, the monolayer film at the backside of the substrate was wiped off carefully with lens tissue soaked with chloroform in order to prevent interference between signals arising from the monolayers at the front and backside of the substrate. In the treatment of data, it was assumed that all the molecules on the quartz substrate have a common tilt angle ϕ with a random azimuthal distribution. The SHG data were analyzed by the general procedure described by Ashwell et al.[19]

Crystal Structure Determination. Crystals of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ were obtained by slow diffusion of diethyl ether vapor into their dichloromethane solution. A brown crystal of dimensions 0.40 × 0.25 × 0.05 mm mounted on a glass fiber was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation. The images were interpreted and intensities integrated using the program DENZO.[20a] The space group was determined on the basis of a statistical analysis of intensity distribution, the successful refinement of the structure was solved by direct methods (SIR92[20b]) and expanded by the Fourier method, and refinement was by full-matrix least-squares using the software package TeXsan[20c] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of two independent formula units. Two of the F atoms of one of the PF$_6^-$ were disordered with F(3) and F(3′) each having an occupation number of 0.5 and F(6) and F(6′) having occupation numbers of 0.7 and 0.3, respectively. In the least-squares refinement, 106 non-H atoms were refined anisotropically, the 14 F atoms were refined isotropically, and 106 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Crystal and structure determination data are summarized in Table 1.

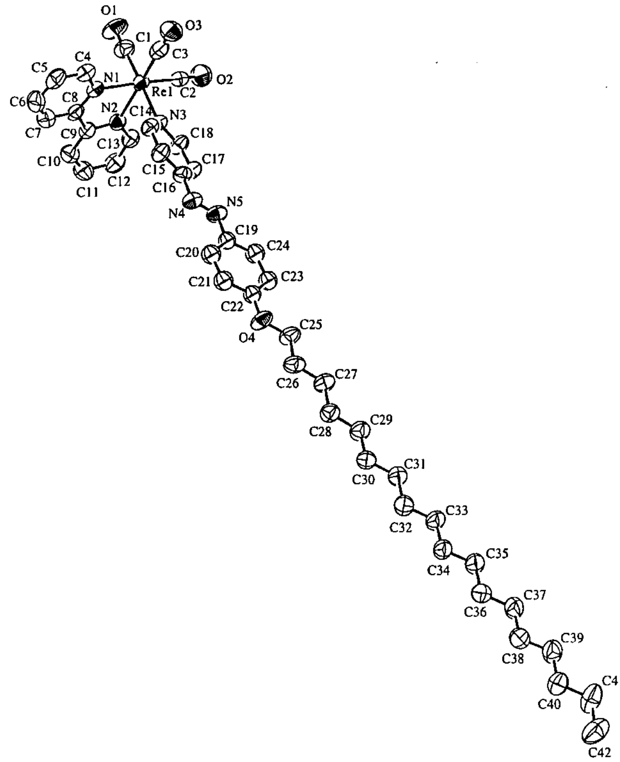

Figure 1. Perspective drawing of one of the complex cations of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 50% probability level.

Results and Discussion

Syntheses and Characterization. All the Re(I) complexes were synthesized by modification of a literature procedure[10,17] and characterized by ^{1}H NMR, IR, positive-ion FAB-MS, and elemental analyses. The structure of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ was determined by X-ray crystallography, in which the *trans* configuration of the azopyridyl group in the ligand was established. The *trans* configuration of the stilbazole unit in *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$ has also been confirmed by ^{1}H NMR spectroscopy, in which the coupling constant of the two olefinic hydrogens of 16 Hz is typical of that for *trans*-alkenes. All the complexes show three intense

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(18) (a) Dougherty, J. P.; Kurtz, S. K. *J. Appl. Crystallogr.* **1976**, *9*, 145. (b) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Peterson, I. R.; Ahmad, M. M.; Neal, D. B.; Petty, M. C.; Roberts, G. G.; Feast, W. J. *J. Opt. Soc. Am.* **1987**, *B4*, 950.

(19) Ashwell, G. J.; Hargreaves, R. C.; Baldwin, C. E.; Bahra, G. S.; Brown, C. R. *Nature* **1992**, *357*, 393.

(20) (a) *DENZO*: *The HKL Manual*—A description of programs *DENZO, XDISPLAYF*, and *SCALEPACK* written by Gewirth, D. with the cooperation of the program authors Otwinowski, Z., and Minor, W., Yale University: New Haven, 1995. (b) *SIR92*: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435. (c) *TeXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$

Re(1)−N(1)	2.183(5)	Re(1)−N(2)	2.179(6)
Re(1)−N(3)	2.222(6)	Re(1)−C(1)	1.934(10)
Re(1)−C(2)	1.932(8)	Re(1)−C(3)	1.926(10)
O(1)−C(1)	1.144(9)	O(2)−C(2)	1.120(8)
O(3)−C(3)	1.153(10)	N(4)−N(5)	1.261(8)
N(1)−Re(1)−N(2)	75.4(2)	N(1)−Re(1)−N(3)	86.0(2)
N(1)−Re(1)−C(1)	92.9(3)	N(1)−Re(1)−C(2)	173.9(3)
N(1)−Re(1)−N(3)	98.7(3)	N(2)−Re(1)−N(3)	82.2(2)
N(2)−Re(1)−C(1)	95.3(3)	N(2)−Re(1)−C(2)	99.0(3)
N(2)−Re(1)−C(3)	173.2(3)	N(3)−Re(1)−C(1)	177.5(3)
N(3)−Re(1)−C(2)	95.6(3)	N(3)−Re(1)−C(3)	94.0(3)
C(1)−Re(1)−C(2)	85.3(3)	C(1)−Re(1)−C(3)	88.4(3)
C(2)−Re(1)−C(3)	87.0(3)	N(5)−N(4)−C(16)	111.1(6)
N(4)−N(5)−C(19)	114.8(6)		

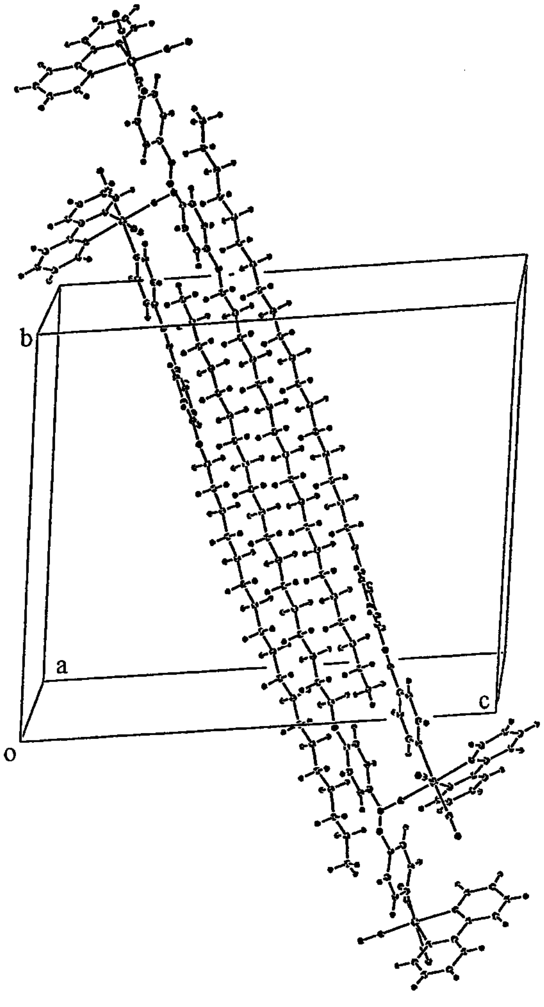

Figure 2. Packing diagram of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ in the unit cell, showing the head-to-tail arrangement of the long aliphatic hydrocarbons of two pairs of complex cations. The disordered PF$_6^-$ ions have been omitted for clarity.

IR absorption bands at ca. 1900−2100 cm^{-1}, typical of the tricarbonyl Re(I) moiety in the facial arrangement.[21]

Crystal Structure. The perspective drawing of the complex cation of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ is shown in Figure 1. Selected bond distances and angles are given in Table 2. The perspective drawing of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ in the unit cell is shown in Figure 2.

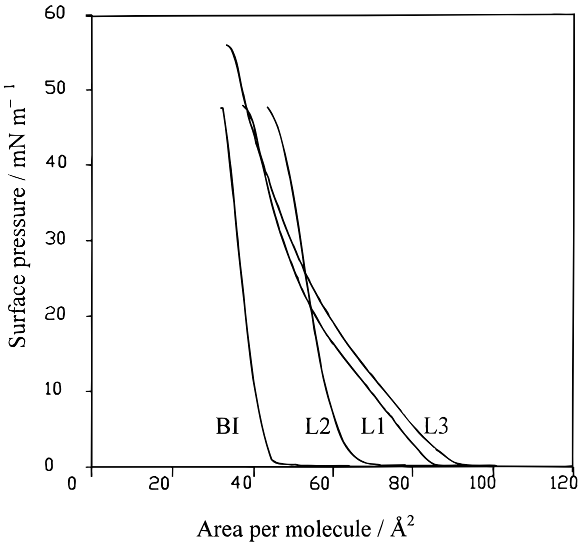

Figure 3. Surface pressure−area (π−*A*) isotherms of *fac*-[Re(CO)$_3$(bpy)(L)]PF$_6$ (L = L1, L2, L3) and BI.

The coordination geometry at the Re atom is distorted octahedral with the three carbonyl ligands arranged in a facial fashion, which is similar to that found in other related rhenium(I) systems.[21] The hydrophobic aliphatic chain is running along an axis that is almost perpendicular to the plane containing the Re atom and the bipyridine unit. The complex *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ crystallizes in the centrosymmetric space group $P\bar{1}$. As seen in Figure 2, the long hydrocarbon chains of the two adjacent neighboring complex cations are arranged in a head-to-tail fashion, which leads to centrosymmetry and therefore the lack of SHG capability of the complex in the crystal form.

Surface Pressure−Area (π−*A*) Isotherms. π−A isotherms for the complexes are shown in Figure 3. All curves show one well-defined condensed region with surface pressure > 30 mN m^{-1} and a collapse pressure of ca. 50 mN m^{-1}, indicative of the stable air−water interface behavior of the complexes. The molecular areas obtained by the extrapolation of the condensed region to zero surface pressure (61 Å^2/molecule for *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$, 63 Å^2/molecule for both *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ and *fac*-[Re(CO)$_3$(bpy)(L3)]PF$_6$) are found to be very close to the calculated values (55 Å^2) based on the crystal structure of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$, suggesting that the complex molecules are packed closely in the film.

Electronic Absorption Spectroscopy. Figure 4 depicts the UV−vis spectra of the complexes in dichloromethane and in LB films. The electronic absorption spectra of all the complexes show an intense absorption at ca. 350−450 nm in dichloromethane at 298 K. With reference to previous spectroscopic work on related rhenium(I) diimine systems,[9,10,17,22] this absorption band is most likely assigned as the dπ(Re) → π*(bpy) metal-to-ligand charge-transfer (MLCT) transition. The observation of an extinction coefficient on the order of 10^4 dm^3 mol^{-1} cm^{-1} for this band, which is much larger than an order of 10^3 dm^3 mol^{-1} cm^{-1} commonly observed for rhenium(I) diimine MLCT transition, is suggestive of a spectral assignment of the band as consisting of an admixture of intraligand (IL) π → π* and MLCT

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(21) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.

Table 3. Photophysical Data of Re(I) Diimine Complexes

compound	medium (*T*/K)	absorption λ_{max}/nm ($\epsilon \times 10^{-4}$/dm^3 mol^{-1} cm^{-1})	emission λ_{em}/nm (τ_0/μs)
[Re(CO)$_3$(bpy)(L1)]PF$_6$	CH$_2$Cl$_2$ (298)	396 (3.36)	554
	LB film	388	*c*
	glass (77)[a]	*b*	492
[Re(CO)$_3$(bpy)(L2)]PF$_6$	CH$_2$Cl$_2$ (298)	370 (2.92)	540
	LB film	366	530
	glass (77)[a]	*b*	492
[Re(CO)$_3$(bpy)(L3)]PF$_6$	CH$_2$Cl$_2$ (298)	366 (3.47)	549 (1.63)
	LB film	350	551
	glass (77)[a]	*b*	495, 527, 560

[a] All glasses are 4:1 (v/v) ethanol−methanol mixture. [b] Not measured. [c] Too weak to be measured.

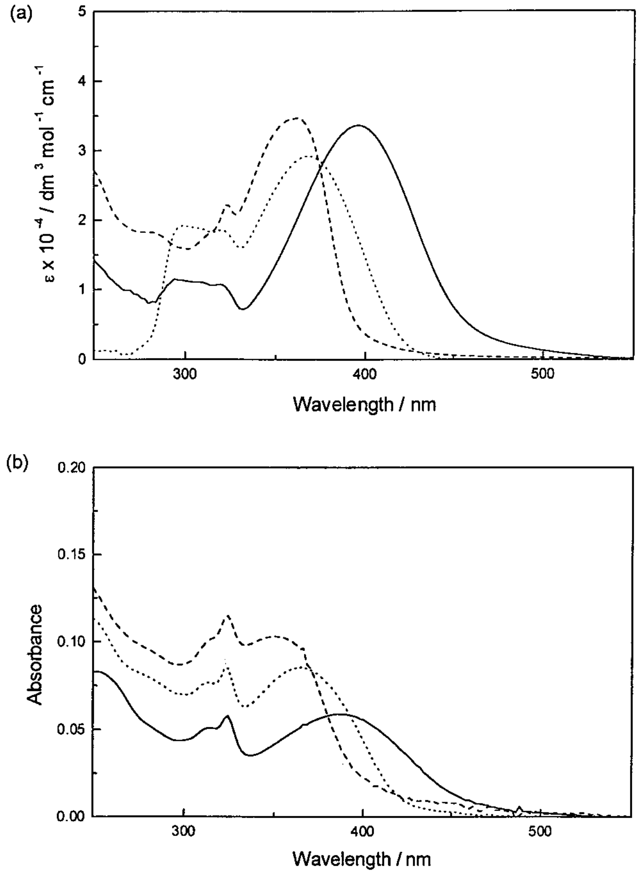

Figure 4. UV−vis spectra of *fac*-[Re(CO)$_3$(bpy)(L)]PF$_6$ where L = L1 (—), L2 (···) and L3 (- - -) (a) in CH$_2$Cl$_2$, (b) in LB films.

character. The electronic absorption spectra of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ in LB films as a function of layer number are shown in Figure 5. A linear relationship between the absorbance at 388 nm and the number of layers deposited on the quartz substrate is observed, indicative of the good deposition behavior of the complex. A blue shift of the low-energy absorption band is observed in the UV−vis spectra of the complexes in the LB film relative to that in fluid solution and is attributed to rigidochromic effects,[23] which are commonly reported in the Re(I) diimine systems.

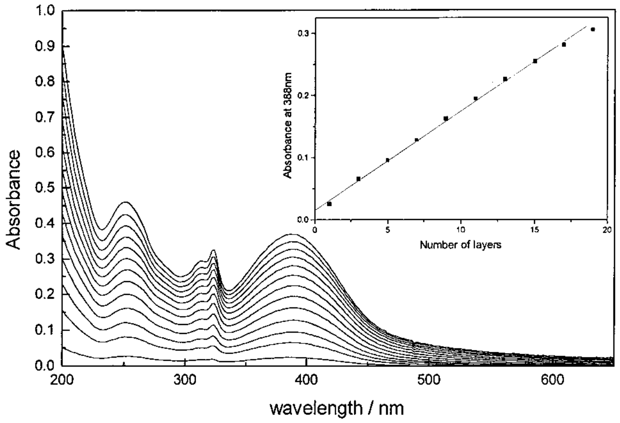

Figure 5. UV−vis spectral traces of *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ deposited on a quartz substrate as a function of layer number. The inset shows the absorbance at 388 nm as a function of layer number.

Emission Spectroscopy. Emission data for the complexes in various media are summarized in Table 3. The emission spectra exhibit a broad band centered at ca. 490−560 nm, attributed to the triplet MLCT emission, typical of Re(I) diimine complexes.[9,10,17,22] The emission energies of the complexes at 77 K glass state and in LB films were found to be blue-shifted with respect to that in fluid solution, attributed to the phenomenon of luminescence rigidochromism.[23] Figure 6 shows the emission spectra of *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$ in various media. The emission spectrum of *fac*-[Re(CO)$_3$(bpy)(L3)]PF$_6$ at 77 K glass state shows vibronic structures with progressional spacing of ca. 1220 cm^{-1}, typical of the ring C−H deformation vibrations in the ground state. This is suggestive of the involvement of both the bipyridine and ligand L3 in the excited state, supporting the assignment of an emission origin of mixed MLCT/IL character.

Second-Harmonic Generation (SHG). The SHG results of the Re(I) complexes are summarized in Table 4. The first-order hyperpolarizability (β) of *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$ is found to be 1.4−1.5 times that of its structurally related organic counterpart, (*E*)-*N*-methyl-4-(2-(4-octadecyloxyphenyl)ethenyl)pyridinium iodide (BI), which has a β value of 1.5×10^{-28} esu.[24] The SHG

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(22) (a) Leasure, R. M.; Sacksteder, L.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *31*, 3722. (b) Zipp, A. P.; Sacksteder, L.; Streich, J.; Cook, A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1993**, *32*, 5629. (c) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335. (d) Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1993,** *65*, 3480. (e) Bacon, J. R.; Demas, J. N. *Anal. Chem.* **1987**, *59*, 2780. (f) Carraway, E. R.; Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1991**, *63*, 337. (g) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448. (h) Chen, P.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271. (i) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285.

(23) (a) Dominey, R. N.; Hauser, B.; Hubbard, J.; Dunham, J. *Inorg. Chem.* **1991**, *30*, 4754. (b) Sullivan, B. P. *J. Phys. Chem.* **1989**, *93*, 24. (c) Lees, A. J. *Comments Inorg. Chem.* **1995**, *17*, 319.

(24) Lupo, D.; Prass, W.; Scheunemann, U.; Laschewsky, A.; Ringsdorf, H.; Ledoux, I. *J. Opt. Soc. Am.* **1988**, *B5*, 300.

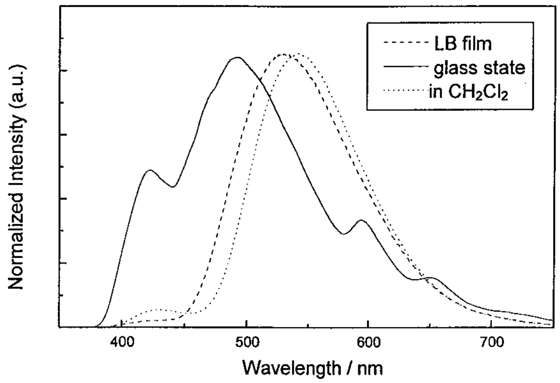

Figure 6. Normalized emission spectra of *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$: (—) at glass state (77 K); (- - -) in LB film; (···) in CH_2Cl_2.

Table 4. First-Order Molecular Hyperpolarizability and Absorbance Maximum of Re(I) Diimine Complexes in Langmuir–Blodgett Films

	UV–vis spectra		relative SHG
compound	λ_{max}/nm	abs per layer	β(complex)/β(BI)[a]
[Re(CO)$_3$(bpy)(L1)]PF$_6$	388	0.012	1.7–2.3
[Re(CO)$_3$(bpy)(L2)]PF$_6$	366	0.017	1.4–1.5
[Re(CO)$_3$(bpy)(L3)]PF$_6$	350	0.021	0.7

[a] BI = (*E*)-*N*-methyl-4-(2-(4-octadecyloxyphenyl)ethenyl)pyridinium iodide.

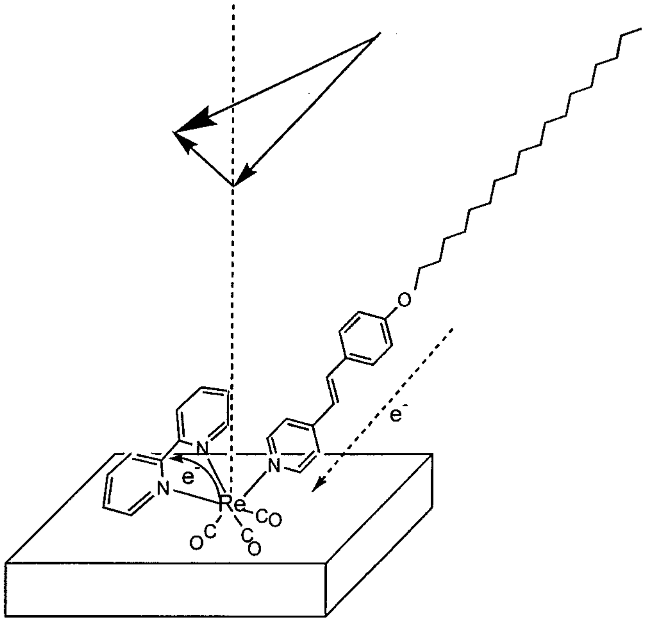

Figure 7. Schematic drawing of the proposed model of *fac*-[Re(CO)$_3$(bpy)(L2)]PF$_6$ on a quartz substrate and the illustration of the charge-transfer contribututions to the resultant dipole moment.

capability of BI has been ascribed to the donor–acceptor charge transfer resulting from the electron donation of the alkoxy group to the pyridinium unit. It is likely that in the present system two types of charge transfer exist and occur along different directions, the resultant of which contributes to the observed hyperpolarizability (Figure 7). One is the Re(I) → bpy metal-to-ligand charge transfer (MLCT), which occurs in the plane of the Re(I) atom and the bipyridine unit. The other is the ligand-centered charge transfer similar to BI, which occurs along the backbone of the ligand L and perpendicular to the Re–bpy plane. Although they act in different directions, it is likely that the dipole moment in the resultant is enhanced, leading to an increase in the first-order hyperpolarizability relative to that of BI.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and a full list of bond distances and angles for *fac*-[Re(CO)$_3$(bpy)(L1)]PF$_6$ are deposited as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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