Inorganic Chemistry

Article

Synthesis and Characterization of Luminescent Rhenium(I) Tricarbonyl Diimine Complexes with a Triarylboron Moiety and the Study of Their Fluoride Ion-Binding Properties

Siu-Tung Lam, Nianyong Zhu, and Vivian Wing-Wah Yam*

Centre for Carbon-Rich Molecular and Metal-Based Materials Research and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China

A series of alkynylrhenium(I) tricarbonyl diimine complexes with a triarylboron moiety has been synthesized and characterized. The binding properties of the complex toward fluoride ions have been studied using electronic absorption and emission spectroscopy and were further supported by ^{19}F NMR binding experiments.

Introduction

With the growing interest in the search for new advanced materials that show novel responsive behavior and improved properties, a variety of investigations into triarylboron have emerged.[1] Because of their high Lewis acidity and electron-accepting ability, this kind of materials has been found to show potential applications in nonlinear optics,[2] organic light-emitting diodes (OLEDs),[3] and particularly in anion sensing.[4−6] By introducing an electron-rich guest to the triarylboron system, the $p_\pi-\pi^*$ conjugation through the vacant p-orbital of the boron atom can be perturbed, and this provides an opportunity to modify the electronic properties of these systems. In spite of

*To whom correspondence should be addressed. E-mail: wwyam@hku. hk. Fax: +(852) 2857-1586. Phone: +(852) 2859-2153.

(1) (a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. (b) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527. (c) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927. (d) Jäkle, F. Boron: Organoboranes. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, 2005. (e) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (f) Hudson, Z. M.; Wang, S. Impact of Donor-Acceptor Geometry and Metal Chelation on Photophysical Properties and Applications of Triarylboranes. *Acc. Chem. Res.* [Online early access]. DOI: 10.1021/ar900072u. Published Online: June 26,2009.

(2) (a) Branger, C.; Lequan, M.; Lequan, R. M.; Barzoukas, M.; Fort, A. *J. Mater. Chem.* **1996**, *6*, 555. (b) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. *J. Solid State Chem.* **2000**, *154*, 5. (c) Liu, Z.-Q.; Fang, Q.; Cao, D.-X.; Wang, D.; Xu, G.-B. *Org. Lett.* **2004**, *6*, 2933. (d) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68. (e) Charlot, M.; Porres, L.; Entwistle, C. D.; Beeby, A.; Marder, T. B.; Blanchard-Desce, M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 600. (f) Yuan, Z.; Entwistle, C. D.; Collings, J. C.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Taylor, N. J.; Kaiser, H. M.; Kaufmann, D. E.; Poon, S.-Y.; Wong, W.-Y.; Jardin, C.; Fathallah, S.; Boucekkine, A.; Halet, J.-F.; Marder, T. B. *Chem. Eur. J.* **2006**, *12*, 2758. (g) Stahl, R.; Lambert, C.; Kaiser, C.; Wortmann, R.; Jakober, R. *Chem. Eur. J.* **2006**, *12*, 2358. (h) Collings, J. C.; Poon, S.-Y.; Le Droumaguet, C.; Charlot, M.; Katan, C.; Pålsson, L.-O.; Beeby, A.; Mosely, J. A.; Kaiser, H. M.; Kaufmann, D.; Wong, W.-Y.; Blanchard-Desce, M.; Marder, T. B. *Chem. Eur. J.* **2009**, *15*, 198.

(3) (a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021. (b) Chen, B.; Zhang, X. H.; Lin, X. Q.; Kwong, H. L.; Wong, N. B.; Lee, C. S.; Gambling, W. A.; Lee, S. T. *Synth. Met.* **2001**, *118*, 193. (c) Kinoshita, M.; Hiroshi, K.; Shirota, Y. *Adv. Funct. Mater.* **2002**, *12*, 780. (d) Jia, W.-L.; Bai, D.-R.; McCormick, T.; Liu, Q.-D.; Motala, M.; Wang, R.-Y.; Seward, C.; Tao, Y.; Wang, S. *Chem. Eur. J.* **2004**, *10*, 994. (e) Liu, Q.-D.; Mudadu, M. S.; Thummel, R.; Tao, Y.; Wang, S. *Adv. Funct. Mater.* **2005**, *15*, 143. (f) Jia, W. L.; Moran, M. J.; Yuan, Y.-Y.; Lu, Z. H.; Wang, S. *J. Mater. Chem.* **2005**, *15*, 3326. (g) Jia, W. L.; Feng, X. D.; Bai, D. R.; Lu, Z. H.; Wang, S.; Vamvounis, G. *Chem. Mater.* **2005**, *17*, 164. (h) Mazzeo, M.; Vitale, V.; Della Sala, F.; Anni, M.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2005**, *17*, 34. (i) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281. (j) Yu, J.-S.; Lou, S.-L.; Jiang, Y.-D.; Li, L.; Li, Q.; Zhan, X.-W. *Proc. SPIE, Int. Soc. Opt. Eng.* **2007**, 6722. (k) Tanaka, D.; Takeda, T.; Chiba, T.; Watanabe, S.; Kido, J. *Chem. Lett.* **2007**, *36*, 262.

(4) (a) Cooper, C. R.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, 1365. (b) Shiratori, H.; Ohno, T.; Nozaki, K.; Osuka, A. *Chem. Commun.* **1999**, 2181. (c) Miyata, M.; Chujo, Y. *Polym. J.* **2002**, *34*, 967. (d) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036. (e) Solé, S.; Gabbaï, F. P. *Chem. Commun.* **2004**, 1284. (f) Melaimi, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 9680. (g) Koskela, S. J. M.; Fyles, T. M.; James, T. D. *Chem. Commun.* **2005**, 945. (h) Liu, Z.-Q.; Shi, M.; Li, F.-Y.; Fang, Q.; Chen, Z.-H.; Yi, T.; Huang, C.-H. *Org. Lett.* **2005**, *7*, 5481. (i) Agou, T.; Kobayashi, J.; Kawashima, T. *Org. Lett.* **2005**, *7*, 4373. (j) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495. (k) Hudnall, T. W.; Melaimi, M.; Gabbaï, F. P. *Org. Lett.* **2006**, *8*, 2747. (l) Liu, X. Y.; Bai, D. R.; Wang, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5475. (m) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879. (n) Chiu, C.-W.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2006**, *128*, 14248. (o) Lee, M. H.; Agou, T.; Kobayashi, J.; Kawashima, T.; Gabbaï, F. P. *Chem. Commun.* **2007**, 1133. (p) Bai, D.-R.; Liu, X.-Y.; Wang, S. *Chem. Eur. J.* **2007**, *13*, 5713. (q) Hudnall, T. W.; Kim, Y.-M.; Bebbington, M. W. P.; Bourissou, D.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2008**, *130*, 10890. (r) Zhou, G.; Baumgarten, M.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 12477. (s) Zhao, S.-B.; Wucher, P.; Hudson, Z. M.; McCormick, T. M.; Liu, X.-Y.; Wang, S.; Feng, X.-D.; Lu, Z.-H. *Organometallics* **2008**, *27*, 6446.

(5) (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372. (b) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816. (c) Sundararaman, A.; Venkatasubbaiah, K.; Victor, M.; Zakharov, L. N.; Rheingold, A. L.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 16554. (d) Yuan, M.-S.; Liu, Z.-Q.; Fang, Q. *J. Org. Chem.* **2007**, *72*, 7915.

(6) (a) Sakuda, E.; Funahashi, A.; Kitamura, N. *Inorg. Chem.* **2006**, *45*, 10670. (b) Zhao, S.-B.; McCormick, T.; Wang, S. *Inorg. Chem.* **2007**, *46*, 10965. (c) Sun, Y.; Ross, N.; Zhao, S.-B.; Huszarik, K.; Jia, W.-L.; Wang, R.-Y.; Macartney, D.; Wang, S. *J. Am. Chem. Soc.* **2007**, *129*, 7510. (d) You, Y.; Park, S. Y. *Adv. Mater.* **2008**, *20*, 3820. (e) Zhao, Q.; Li, F.-Y.; Liu, S.-J.; Yu, M.-X.; Liu, Z.-Q.; Yi, T.; Huang, C.-H. *Inorg. Chem.* **2008**, *47*, 9256.

the growing interest in this area, most of the works are focused on the studies of organic systems,[4,5] with transition metal complex systems less extensively explored despite numerous works on metal complexes with rich spectroscopic properties being known.[6] A particular class of transition metal complexes that has aroused immense interest is the luminescent rhenium(I) tricarbonyl diimine complexes that show rich and promising photophysical properties.[7] The metal-to-ligand charge-transfer (MLCT) excited states of these luminescent organometallic systems are well documented to show large responsive changes toward host−guest complexation.[8] Although there have been some studies reporting the incorporation of the triarylboron moiety into Pt(II) and Ir(III) MLCT complexes, most of the reported complexes are connected to the boron moiety through the polypyridine ligands.[6] It is envisaged that upon incorporation of the triarylboron moiety through an alkynyl ligand to the rhenium(I) complexes, the rich photophysical properties of the MLCT excited state of these metal complex systems may be capable of serving as versatile spectroscopic reporters and probes for the fluoride ion. Interestingly, the use of rhenium(I) tricarbonyl diimine complexes for anion sensing is relatively less explored when compared with cation sensing and other metal complex systems.[9] Herein, we report the synthesis of triarylboron-containing rhenium(I) tricarbonyl diimine complexes and their anion-binding properties for fluoride ion.

Experimental Details

All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. The solvents were

Scheme 1. Synthesis of Complexes **1**−**3**

N∩N = 2,9-Me$_2$phen (**1**), phen (**2**), 5,6-Br$_2$phen (**3**)
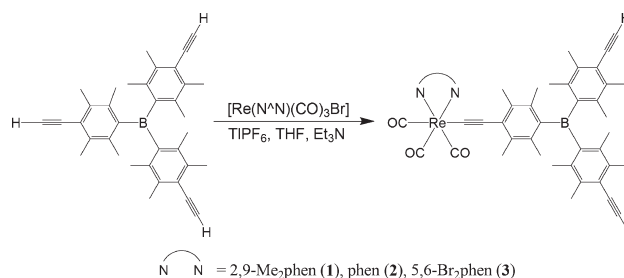
dried and freshly distilled before use. The rhenium(I) complex precursors[10] and tris(4-ethynyl-2,3,5,6-tetramethylphenyl)-borane[11] were synthesized according to reported procedures or with slight modifications. Other materials and reagents were of analytical grade and were used without further purification.

Synthesis and Characterization of the Rhenium(I) Complexes 1−3. **[Re(CO)$_3$(2,9-Me$_2$phen)(C≡C−C$_6$Me$_4$-B(C$_6$Me$_4$-C≡C-H)$_2$)] (1).** This was prepared by modification of a previously reported procedure for related alkynylrhenium(I) tricarbonyl diimine complexes (Scheme 1).[7g,12] A mixture of [Re(CO)$_3$(2,9-Me$_2$phen)Br] (200 mg, 0.36 mmol), TlPF$_6$ (138 mg, 0.39 mmol), and tris(4-ethynyl-2,3,5,6-tetramethylphenyl)borane (260 mg, 0.54 mmol) in THF (100 mL) was heated under reflux in an inert atmosphere of nitrogen in the presence of Et$_3$N (5 mL) for 48 h. The yellowish orange suspension was then filtered to remove the insoluble TlBr, and the orange filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel using dichloromethane as eluent. The second band, which contains the desired product, was collected and evaporated to dryness. Subsequent recrystallization by layering hexane onto a concentrated dichloromethane solution of the product gave **1** as analytically pure orange crystal. Yield: 90 mg, 26%. ^{1}H NMR (400 MHz, CD$_3$CN, 298 K, relative to Me$_4$Si): δ 1.58 (s, 6H, −CH$_3$), 1.68 (s, 6H, −CH$_3$), 1.80 (s, 12H, −CH$_3$), 2.26 (s, 12H, −CH$_3$), 3.29 (s, 6H, −CH$_3$), 3.79 (s, 2H, −C≡CH), 7.86 (d, J = 8.2 Hz, 2H, 3- and 8-phenanthrolinyl H's), 7.99 (s, 2H, 5- and 6-phenanthrolinyl H's), 8.50 (d, J = 8.2 Hz, 2H, 4- and 7-phenanthrolinyl H's). Positive FAB-MS: m/z 959 [M]$^+$, 931 [M−CO]$^+$. IR (KBr disk, ν/cm^{-1}): 1883 (s), 1903 (s), 2003 (s) ν(C≡O) ; 2091 (w) ν(C≡C), 2202 (w) ν(C≡C). Elemental analyses. Found (%): C 66.12, H 5.24, N 2.78. Calcd for **1**: C 66.36, H, 5.04, N 2.92.

[Re(CO)$_3$(phen)(C≡C−C$_6$Me$_4$-B(C$_6$Me$_4$−C≡CH)$_2$)] (2). This was prepared according to a procedure similar to that described for **1**, except [Re(CO)$_3$(phen)Br] (170 mg, 0.33 mmol) was used in place of [Re(CO)$_3$(2,9-Me$_2$phen)Br] to give **2** as orange crystals. Yield: 80 mg, 24%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 1.58 (s, 6H, −CH$_3$), 1.68 (s, 6H, −CH$_3$), 1.80 (s, 12H, −CH$_3$), 2.26 (s, 12H, −CH$_3$), 3.79 (s, 2H, −C≡CH), 7.75 (m, 2H, 3- and 8-phenanthrolinyl H's), 7.96 (s, 2H, 5- and 6-phenanthrolinyl H's), 8.45 (d, J = 8.2 Hz, 2H, 4- and 7-phenanthrolinyl H's), 9.41 (d, J = 5.1 Hz, 2H, 2- and 9-phenanthrolinyl H's). Positive FAB-MS: m/z 930 [M]$^+$, 902 [M−CO]$^+$. IR (KBr disk, ν/cm^{-1}): 1876 (s), 1911 (s), 2004 (s) ν(C≡O) ; 2095 (w) ν(C≡C), 2202 (w) ν(C≡C). Elemental analyses. Found (%): C 65.52, H 5.35, N 2.75. Calcd for **2**: C 65.50, H 5.17, N 2.99.

[Re(CO)$_3$(5,6-Br$_2$phen)(C≡C−C$_6$Me$_4$-B(C$_6$Me$_4$−C≡CH)$_2$)] (3). This was prepared according to a procedure similar to that described for **1**, except [Re(CO)$_3$(5,6-Br$_2$phen)Br] (230 mg, 0.33 mmol) was used in place of [Re(CO)$_3$(2,9-Me$_2$phen)Br] to give **3**

(7) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 3931. (c) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790. (d) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597. (e) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (f) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (g) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1995**, *14*, 2749. (h) Yam, V. W.-W. *Chem. Commun.* **2001**, 789. (i) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734. (j) Ko, C.-C.; Wu, L.-X.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Chem. Eur. J.* **2004**, *10*, 766. (k) Lee, P. H.-M.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2007**, *129*, 6058. (l) Lam, S.-T.; Wang, G.-X.; Yam, V. W.-W. *Organometallics* **2008**, *27*, 4545. (m) Wong, K. M.-C.; Lam, S. C.-F.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W.; Roue, S.; Lapinte, C.; Fathallah, S.; Costuas, K.; Kahlal, S.; Halet, J.-F. *Inorg. Chem.* **2003**, *42*, 7086. (n) Chong, S. H.-F.; Lam, S. C.-F.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K.; Fathallah, S.; Costuas, K.; Halet, J.-F. *Organometallics* **2004**, *23*, 4924.

(8) (a) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108. (b) Shen, Y.; Sullivan, B. P. *Inorg. Chem.* **1995**, *34*, 6235. (c) Yam, V. W.-W.; Wong, K. M.-C.; Lee, V. W.-M.; Lo, K. K.-W.; Cheung, K.-K. *Organometallics* **1995**, *14*, 4034. (d) Shen, Y.; Sullivan, B. P. *J. Chem. Educ.* **1997**, *74*, 685. (e) Uppadine, L. H.; Redman, J. E.; Dent, S. W.; Drew, M. G. B.; Beer, P. D. *Inorg. Chem.* **2001**, *40*, 2860. (f) Sun, S. S.; Lee, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445. (h) Lewis, J. D.; Moore, J. N. *Dalton Trans.* **2004**, 1376. (g) Lazarides, T.; Miller, T. A.; Jeffery, J. C.; Ronson, T. K.; Adams, H.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2005**, 528. (h) Li, M.-J.; Ko, C.-C.; Duan, G.-P.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2007**, *26*, 6091.

(9) (a) Redman, J. E.; Beer, P. D.; Dent, S. W.; Drew, M. G. B. *Chem. Commun.* **1998**, 231. (b) Beer, P. D.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V. *Chem. Commun.* **1999**, 1755. (c) Uppadine, L. H.; Keene, F. R.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2001**, 2188. (d) Cary, D. R.; Zaitseva, N. P.; Gray, K.; O'Day, K. E.; Darrow, C. B.; Lane, S. M.; Peyser, T. A.; Satcher, J. H., Jr.; Van Antwerp, W. P.; Nelson, A. J.; Reynolds, J. G. *Inorg. Chem.* **2002**, *41*, 1662. (e) Beer, P. D.; Sambrook, M. R.; Curiel, D. *Chem. Commun.* **2006**, 2105. (f) Tzeng, B.-C.; Chen, Y.-F.; Wu, C.-C.; Hu, C.-C.; Chang, Y.-T.; Chen, C.-K. *New J. Chem.* **2007**, *31*, 202. (g) Lin, T.-P.; Chen, C.-Y.; Wen, Y.-S.; Sun, S.-S. *Inorg. Chem.* **2007**, *46*, 9201.

(10) (a) Drew, M. G. B.; Davis, K. M.; Edwards, D. A.; Marshalsea, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1098. (b) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorganic syntheses* **1985**, *23*, 41. (c) Black, S. I.; Young, G. B. *Polyhedron* **1989**, *8*, 585.

(11) Yamaguchi, S.; Shirasaka, T.; Tamao, K. *Org. Lett.* **2000**, *2*, 4129.
(12) Liddle, B. J.; Lindeman, S. V.; Reger, D. L.; Gardinier, J. R. *Inorg. Chem.* **2007**, *46*, 8484.

as red microcrystalline solid. Yield: 78 mg, 20%. ^{1}H NMR (400 MHz, CD$_3$CN, 298 K, relative to Me$_4$Si): δ 1.58 (s, 6H, −CH$_3$), 1.68 (s, 6H, −CH$_3$), 1.78 (s, 12H, −CH$_3$), 2.26 (s, 12H, −CH$_3$), 3.79 (s, 2H, −C≡CH), 7.98 (dd, J = 3.9 and 5.1 Hz, 2H, 3- and 8-phenanthrolinyl H's), 9.01 (d, J = 5.1 Hz, 2H, 4- and 7-phenanthrolinyl H's), 9.49 (d, J = 3.9 Hz, 2H, 2- and 9-phenanthrolinyl H's). Positive FAB-MS: m/z 1090 [M]$^+$, 1062 [M−CO]$^+$. IR (KBr disk, v/cm^{-1}): 1890 (s), 1915 (s), 2009 (s) v(C≡O); 2091 (w) v(C≡C), 2202 (w) v(C≡C). Elemental analyses. Found (%): C 53.28, H 4.42, N 2.65. Calcd for **3**·CH$_2$Cl$_2$: C 53.14, H 4.12, N 2.38.

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or a Bruker AV400 (400 MHz) NMR spectrometer at 298 K with chemical shifts (δ, ppm) relative to tetramethylsilane (Me$_4$Si). ^{19}F NMR (376.4 MHz) spectra were recorded on a Bruker AV400 NMR spectrometer at 298 K with chemical shifts (δ, ppm) relative to trichlorofluoromethane (CFCl$_3$). Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

UV−Vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature were recorded on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer. For solution emission and excitation spectra, samples were rigorously degassed with no fewer than four freeze−pump−thaw cycles prior to the measurements.

The electronic absorption spectral titration was performed on a Varian Cary 50 UV−vis spectrophotometer at room temperature while the emission titration was performed on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer. Supporting electrolyte (0.1 M ^{n}Bu$_4$NPF$_6$) was added to maintain a constant ionic strength of the sample solution. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit[13] of the absorbance (A) versus the concentration of the fluoride ion added (c_M) according to the following equation:

$$A = A_o + \frac{A_{lim} - A_o}{2c_o}[c_o + c_M + 1/K_s - [(c_o + c_M + 1/K_s)^2 - 4c_o c_M]^{1/2}]$$ (1)

where A_o and A are the absorbance of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, c_o is the total concentration of the triarylboron-containing rhenium(I) complex, c_M is the concentration of the added fluoride anion, A_{lim} is the limiting value of absorbance at saturation level, and K_s is the stability constant. For emission titration studies, eq 1 can be modified to give eq 2, written as

$$I = I_o + \frac{I_{lim} - I_o}{2c_o}[c_o + c_M + 1/K_s - [(c_o + c_M + 1/K_s)^2 - 4c_o c_M]^{1/2}]$$ (2)

where I_o and I are the emission intensities of the complex at a selected wavelength in the absence and presence of the fluoride ion, respectively, and I_{lim} is the limiting value of emission intensity in the presence of excess fluoride ion.

X-ray Crystallography. Yellow crystals of complexes **1** and **2** with dimensions of 0.3 mm × 0.25 mm × 0.1 mm and 0.6 mm × 0.42 mm × 0.28 mm, respectively, mounted in glass capillary were used for data collection at 28 °C on a Bruker Smart CCD 1000 using graphite monochromatized Mo-K$_α$ radiation ($λ$ = 0.71073 Å). The structures were solved by direct methods

employing the SHELXS-97 program[14] on a PC. Re and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using the program SHELXL-97[15] on a PC. For complex **1**, there was one formula unit in the asymmetric unit. Because of large thermal parameters of the Re(Me$_2$phen)(CO)$_3$ group, the group was treated with disorderness in the mode of shift. The shift started with the Re atom in amount of 0.290 Å, and the ligands shifted at the same time, that is, two sets of positions of the group were located. The ratio of the occupancies at the two positions was found to be 61:39 at the final stage of convergence of the least-squares refinements. Non-H atoms of the first set of the group were refined anisotropically. Only the Re atom of the second set was refined anisotropically, with other non-H atoms of the second set refined isotropically. Restraints were applied to the disordered fragments, assuming the phenanthroline ligand to be flat and the rings to be regular hexagons, with bond lengths of 1.39 Å. The corresponding bond lengths and distances of the Re(Me$_2$phen)(CO)$_3$ group were also assumed to be similar, that is, Re−C, C−O bonds and 1,3-Re···O distances. For complex **2**, there was one formula unit in the asymmetric unit. One chloroform solvent molecule was located with disorderness. The chloroform was disordered into two sets of positions (in the ratio of 67:33). Restraints were applied to the disordered chloroform, assuming similar C−Cl and 1,3-Cl···Cl bond distances. For crystallographic data in CIF, see the Supporting Information.

Results and Discussion

Crystal Structure Determination. Single crystals of **1** and **2** were obtained by layering of hexane onto a concentrated chloroform solution of the respective complex. The structures of complexes **1** and **2** in the solid state are depicted in Figures 1 and 2, respectively, and their crystallographic data are summarized in Table 1. In both cases, the three durene rings of the triarylboron ligand are arranged in a propeller-like fashion, with the dihedral angles between the trigonal planar coordination plane of boron and the planes of the durene rings at 60−66°, and the C−B−C angles close to the ideal 120°.[11] The coordination geometry at the rhenium(I) center is distorted octahedral, with the three carbonyl ligands arranged in a facial fashion. The N−Re−N bond angles of 74.2(5)−76.2(7)° were found to be less than 90°, as required by the bite distance exerted by the steric demand of the chelating phenanthroline ligands, as is commonly found in other related complexes.[7g,h] The C≡C bond lengths were found to be 1.102(17)−1.124(17) Å, typical of those found in other σ-bonded metal alkynyl systems.[7g,h] The Re−C≡C units were essentially linear with a Re−C≡C bond angle of 169.8(4)−172.3(7)°, similar to those found in other related Re(I) alkynyl complex systems.[7g,h]

Photophysical Properties. The electronic absorption spectra of complexes **1**−**3** show intense high-energy absorption bands at about 270−360 nm, ascribed to an admixture of intraligand (IL) $π → π^*$ transitions of the diimine and alkynyl ligands. The low-energy absorptions at about 370−420 nm with extinction coefficients in the

(13) Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.

(14) Sheldrick, G. M. *SHELXS97, SHELX97, Programs for Crystal Structure Analysis* (*Release 97−2*); University of Göttingen: Göttingen, Germany, 1997.

(15) Sheldrick, G. M. *SHELXL97, SHELX97, Programs for Crystal Structure Analysis* (*Release 97−2*); University of Göttingen: Göttingen, Germany, 1997.
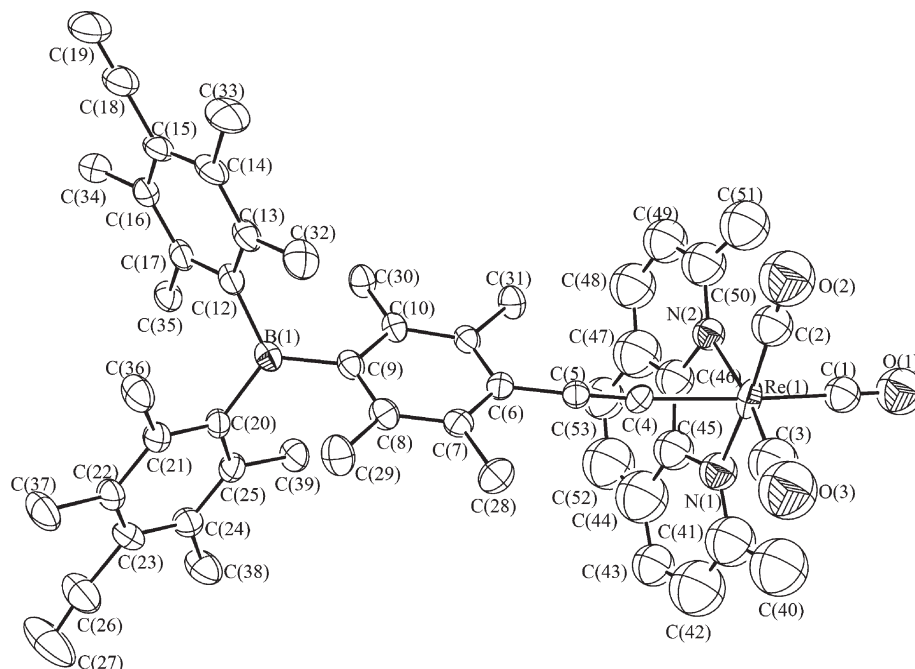
Figure 1. Perspective drawing of complex **1** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.
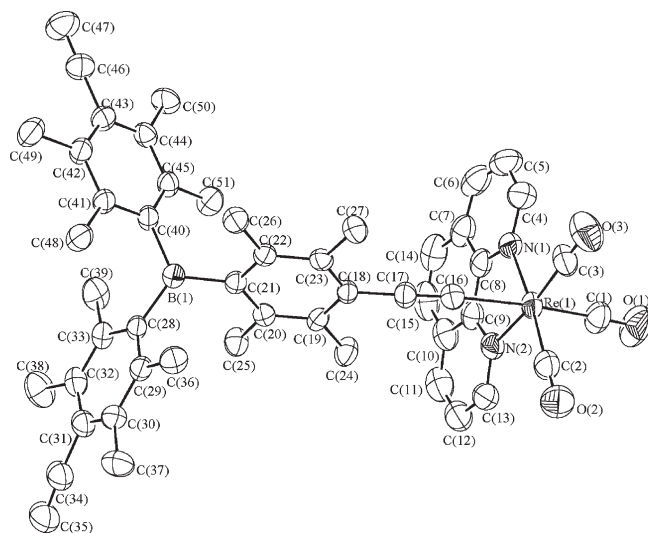

Figure 2. Perspective drawing of complex **2** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

order of 10^4 dm^3 mol^{-1} cm^{-1} were assigned to an admixture of intramolecular charge-transfer transitions from the diarylalkynyl moiety to the triarylboron moiety $[\pi(\text{aryl}) \rightarrow \text{p(B)}]^{11}$ and $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$ metal-to-ligand charge transfer (MLCT) transitions. In addition, low-energy absorption tails at about 420–440 nm with extinction coefficients in the order of 10^3 dm^3 mol^{-1} cm^{-1} were observed, assigned to the $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$ metal-to-ligand charge transfer (MLCT) transition, probably mixed with some $[\pi(\text{C}\equiv\text{CR}) \rightarrow \pi^*(\text{diimine})]$ alkynyl-to-diimine ligand-to-ligand charge transfer

(16) (a) Reichardt, C.; Dimroth, K. *Fortschr. Chem. Forsch.* **1968**, *11*, 1. (b) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. (c) Ng, C.-O.; Lo, L. T.-L.; Ng, S.-M.; Ko, C.-C.; Zhu, N. *Inorg. Chem.* **2008**, *47*, 7447.
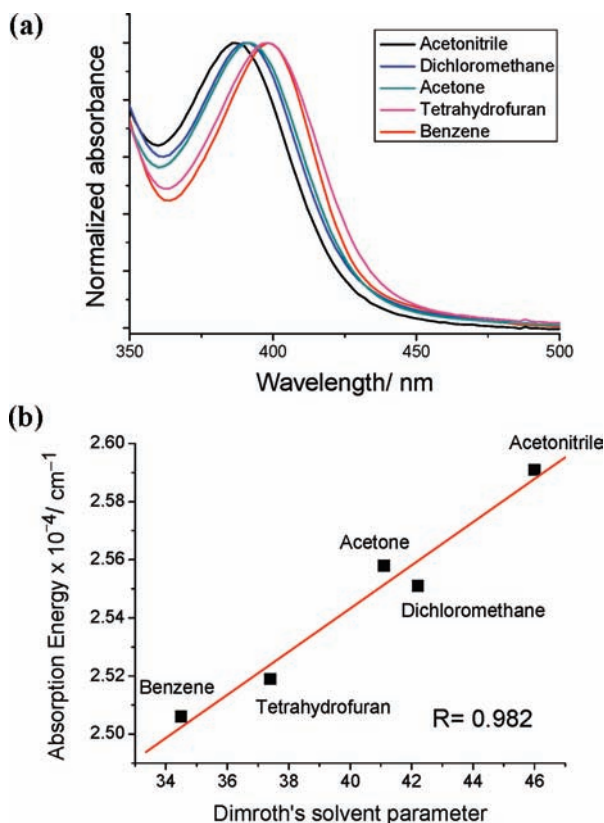
Table 1. Crystal and Structure Determination Data of **1** and **2·**CHCl$_3$

	1	**2·**CHCl$_3$
empirical formula	C$_{53}$H$_{50}$BN$_2$O$_3$Re	C$_{52}$H$_{47}$BCl$_3$N$_2$O$_3$Re
formula weight	959.96	1051.28
temperature	301(2) K	301(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$
a, Å	9.463(2)	13.795(2) Å
b, Å	13.821(2)	14.022(3) Å
c, Å	20.383(4)	24.428(5) Å
α, deg	107.81(2)	90
β, deg	98.15(2)	102.43(2)
γ, deg	92.75(2)	90
volume	2500.6(8) Å^3	4614.5(15) Å^3
Z	2	4
density (calculated)	1.275 g cm^{-3}	1.513 g cm^{-3}
crystal size	0.3 mm × 0.25 mm × 0.1 mm	0.6 mm × 0.42 mm × 0.28 mm
θ range for data collection	2.13 to 25.68°	1.71 to 25.68°
index ranges	$-11 \leq h \leq 11$ $-14 \leq k \leq 16$ $-24 \leq l \leq 24$	$-16 \leq h \leq 16$ $-17 \leq k \leq 15$ $-29 \leq l \leq 29$
reflections collected/unique	15223/9170[R(int) = 0.0206]	26696/8737[R(int) = 0.0200]
Completeness to θ = 25.68°	96.6%	99.7%
goodness-of-fit on F^2	0.944	1.020
final R indices^a [$I > 2\sigma(I)$]	R_1 = 0.0667, wR_2 = 0.2051	R_1 = 0.0344, wR_2 = 0.0928
largest diff. peak and hole (e Å^{-3})	2.200 and -0.792	1.076 and -0.688

^{a} $R_{\text{int}} = \sum||F_o^2 - F_c^2 \text{(mean)}|/\sum[F_o^2]$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

(LLCT) character.^{7g,h,l} The assignment of the origin of the absorption bands was further supported by the solvatochromism studies, with the absorption energy well correlated with the Dimroth's solvent parameter^{16}

Figure 3. (a) Normalized electronic absorption spectra of **1** in different solvents at 298 K. (b) A plot of absorption energy of **1** in different solvents versus Dimroth's solvent parameter and its linear least-squares fit (solid line).

(Figure 3). Negative solvatochromism was observed with non-polar solvents causing a red shift in the MLCT/LLCT transitions in the UV−vis absorption spectra, similar to that of other related rhenium(I) polypyridine systems.[17] It has been reported that this may be due to interactions of the solvent with the charge transfer excited state.[7a,f,18] The electronic absorption data of complexes **1**−**3** are collected in Table 2.

Upon excitation at $\lambda \geq 350$ nm, the complexes displayed a moderately intense emission band in degassed THF solution at 550−750 nm. The long-lived emission with lifetimes in the sub-microsecond range, typical of rhenium(I) tricarbonyl diimine complexes,[7g,h,l] was suggestive of a triplet parentage. With reference to previous spectroscopic studies on other related rhenium(I) alkynyl complexes,[7g,h,l] the luminescence was assigned as derived from excited states of a ^{3}MLCT $[d\pi(Re) \rightarrow \pi^*(diimine)]$ origin, with some mixing of ^{3}LLCT $[\pi(C\equiv CR) \rightarrow \pi^*(diimine)]$ character.

Fluoride-Binding Studies. To explore their potential use in anion recognition, the anion-binding abilities of these alkynylrhenium(I) complexes were explored using UV−vis absorption and emission spectrophotometry.

(17) (a) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. (b) Sullivan, B. P. *J. Phy. Chem.* **1989**, *93*, 24. (c) Xue, W.-M.; Chan, M. C.-W.; Su, Z.-M.; Cheung, K.-K.; Liu, S.-T.; Che, C.-M. *Organometallics* **1998**, *17*, 1622. (d) Heilmann, O.; Hornung, F. M.; Fiedler, J.; Kaim, W. *J. Organomet. Chem.* **1999**, *589*, 2. (e) Knör, G.; Leirer, M.; Vogler, A. *J. Organomet. Chem.* **2000**, *610*, 16.
(18) Pu, Y.-J.; Harding, R. E.; Stevenson, S. G.; Namdas, E. B.; Tedeschi, C.; Markham, J. P. J.; Rummings, R. J.; Burn, P. L.; Samuel, I. D. W. *J. Mater. Chem.* **2007**, *17*, 4255.

Upon addition of F$^-$ ions to a solution of **1** (2.5×10^{-5} M) in acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$), a decrease in the absorbance of the low-energy band was observed. Although the spectral changes in the UV−vis absorption spectra was not very significant (Figure 4a), the dramatic color changes could be readily noticeable by the naked eye as shown in Figure 4b. The detection limit of the F$^-$ ions was found to be $3.8 \pm 0.2 \times 10^{-6}$ M, estimated based on the well-established technique of method detection limit (MDL) as 3σ.[19] Well-defined isosbestic points were obtained and saturation was reached when the concentration of F$^-$ ions was about 3×10^{-5} M. Figure 4a shows the electronic absorption spectral traces of **1** in acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of F$^-$ at 298 K. The inset in Figure 4a showed the titration curve of **1** with F$^-$ ions together with the theoretical fits to the equation for the formation of a 1:1 adduct.[13] Stoichiometry studies indicated that **1** formed 1:1 complexes with F$^-$ ions under the conditions studied, and the results are summarized in Table 3. The log K_s values for the binding of F$^-$ ions to **1** were found to be 5.62, which is comparable to that reported in the literature.[5] The red shift in absorption energies observed upon ion-binding is consistent with the MLCT/LLCT assignment of the low-energy absorption, since the binding of the negatively charged fluoride ion, together with an increased electron-donating ability of the alkynyl ligand upon fluoride ion-binding would cause the MLCT/LLCT transition to occur at lower energies.

The changes in the luminescence response of **1** toward F$^-$ ion were studied upon excitation at the isosbestic wavelength of 430 nm in degassed acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$). The emission spectra showed a diminution of the emission intensities (Figure 5) upon inclusion of the F$^-$ ions, which is similar to their related organic counterparts.[4,5] The inset in Figure 5 showed the emission titration curve of **1** with F$^-$ ions and the theoretical fits to the equation for the formation of a 1:1 adduct.[13] The origin of the emission was assigned to be derived from an excited state of predominantly ^{3}MLCT in character with some mixing of a ^{3}LLCT state, as was commonly observed in other rhenium(I) tricarbonyl diimine systems.[7,8] The decrease in emission intensity could be rationalized by the coordination of fluoride ion to the empty p orbital of the boron atom, which would block the intramolecular charge transfer and interrupt the π conjugation extended through the boron atom, that led to phosphorescence quenching. A log K_s value of 5.61 was obtained for the binding of F$^-$ ions to **1**. This result is in good agreement with that obtained from UV−vis absorption binding studies and further supported the 1:1 complexation mode. Similar findings were observed in complexes **2** and **3**.

In addition, the ion-binding properties of complex **1** have also been probed by ^{19}F NMR spectroscopy by addition of an excess of ^{n}Bu$_4$NF in solution. Two distinct signals were observed at $\delta -120$ ppm and $\delta -151$ ppm, which were assigned to the free fluoride ions and the boron-bound fluoride, respectively, based on the chemical shifts of related compounds reported in the literature.[41] Upon addition of the fluoride ions, dative coordination between the fluoride and the boron atom would

(19) MacDougall, D.; Crummett, W. B. *Anal. Chem.* **1980**, *52*, 2242.

Table 2. Photophysical Data of Complexes **1**−**3**

Complex	Absorption λ_{abs} /nm (ε /dm^{3}mol^{-1}cm^{-1})^a	Medium (T /K)	λ_{em}/nm (τ_o /μs)
[Re(CO)$_3$(2,9-Me$_2$phen)(C≡C−C$_6$Me$_4$-B-(C$_6$Me$_4$−C≡CH)$_2$)] (**1**)	254 (62460), 272 (56190), 328 sh (23825), 398 (25100)	THF (298)	673 (0.37)
		solid (298)	614 (<0.1)
		solid (77)	600 (0.9)
		glass^b (77)	570 (19.8)
[Re(CO)$_3$(phen)(C≡C−C$_6$Me$_4$-B-(C$_6$Me$_4$−C≡CH)$_2$)] (**2**)	254 (50770), 272 (50140), 336 sh (17925), 400 (20905)	THF (298)	690 (0.43)
		solid (298)	620 (<0.1)
		solid (77)	610 (1.0)
		glass^b (77)	582 (8.9)
[Re(CO)$_3$(5,6-Br$_2$phen)(C≡C−C$_6$Me$_4$-B-(C$_6$Me$_4$−C≡CH)$_2$)] (**3**)	248 (47900), 278 (45440), 340 sh (14710), 396 (16675), 448 sh (2475)	THF (298)	730 (0.16)
		solid (298)	694 (<0.1)
		solid (77)	620 (0.3)
		glass^b (77)	588 (13.3)

^{a} In THF. ^{b} Measured in EtOH−MeOH (4:1, v/v) glass.
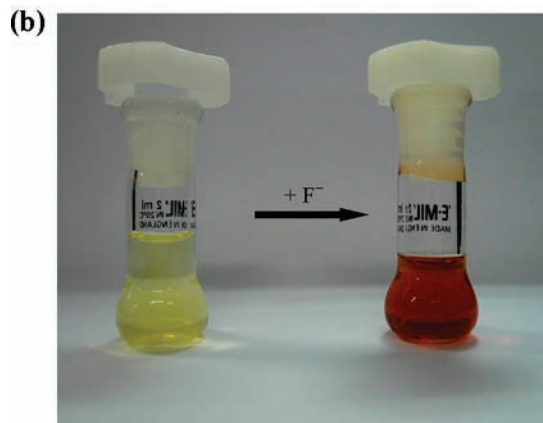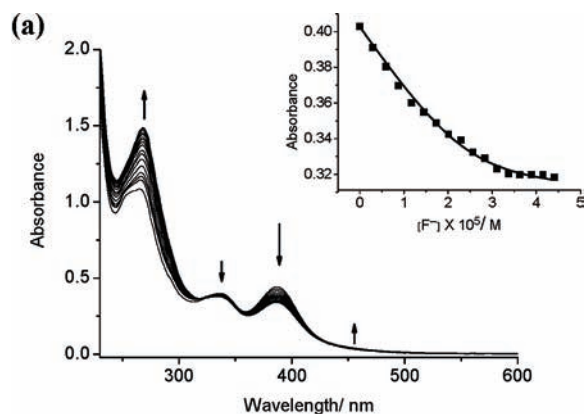
Figure 4. (a) UV−Vis spectral changes of **1** upon addition of various concentrations of ^{n}Bu$_4$NF in CH$_3$CN (0.1 M ^{n}Bu$_4$NPF$_6$). Inset: A plot of absorbance at 386 nm (■) as a function of the concentration of F$^-$ with theoretical fits (solid line) for the 1:1 binding of complex **1** with F$^-$. (b) Photograph showing the color change of **1** before (left) and after (right) the addition of fluoride ion.

Table 3. Binding Constants (log K_s) of Complexes **1**−**3** for Fluoride Ions in Acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$)

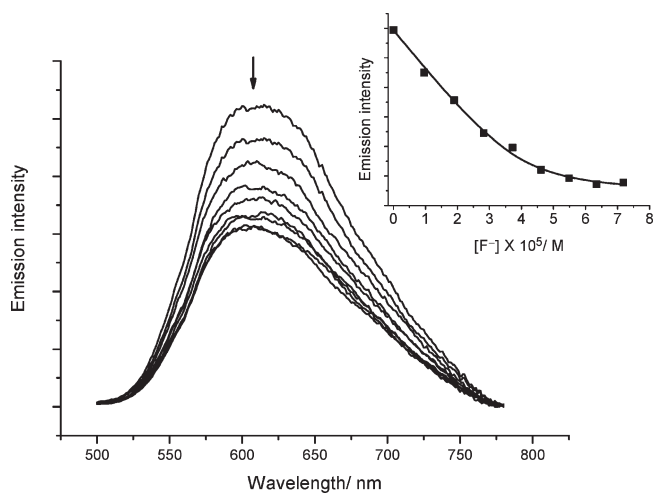|	Log K_s	
Complex	UV−Visible	Emission
1	5.62 ± 0.13	5.61 ± 0.12
2	5.58 ± 0.15	5.58 ± 0.09
3	5.29 ± 0.02	5.28 ± 0.04

Figure 5. Corrected emission spectral changes of **1** upon addition of ^{n}Bu$_4$NF in CH$_3$CN (0.1 M ^{n}Bu$_4$NPF$_6$). Inset: A plot of emission intensity upon excitation at 430 nm (■) as a function of the concentration of F$^-$ with theoretical fits (solid line) for the 1:1 binding of complex **1** with F$^-$.
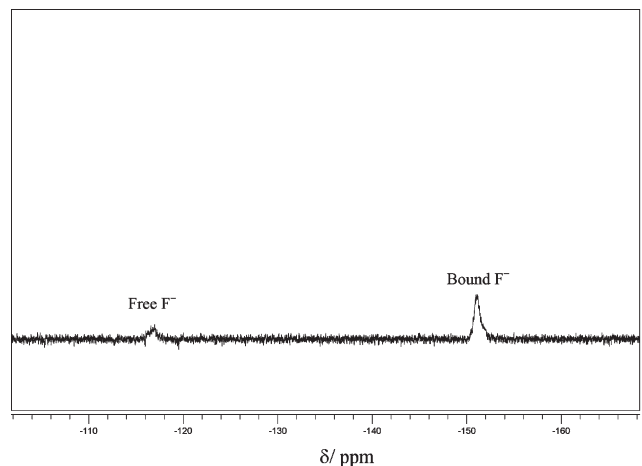

Figure 6. ^{19}F NMR spectrum of **1** in the presence of an excess of ^{n}Bu$_4$NF in CD$_3$CN.

decrease the electron density at the fluoride, causing a downfield shift of the signal (Figure 6).

Conclusion

In conclusion, an alkynylrhenium(I) tricarbonyl diimine system was found to be capable of binding F^- ions with spectral changes in the UV−vis absorption and emission spectra, and was further supported by ^{19}F NMR binding experiment, which may find interesting applications in the design of spectrochemical and luminescence chemosensors.

Supporting Information Available: X-ray crystallographic data in CIF format of complexes **1** and **2**, table summarizing data of absorption maxima of **1**−**3** and Dimroth's solvent parameter, and normalized absorption spectra in different solvents at 298 K and titration spectra with fitting curves of complexes **2**−**3** upon addition of fluoride ions by UV−vis and emission spectroscopic methods. This material is available free of charge via the Internet at http://pubs.acs.org.