

# Synthesis and optical properties of metal-centered dimeric fullerene macromolecules<sup>☆</sup>

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## Abstract

Dimeric fullerene macromolecules were prepared via the complexation of two fullerenedylated 2,2':6',2''-terpyridine ligands with Fe(II) and Co(II) ions. The solubility of these macromolecules in some organic solvents allowed both their structural characterization and a study of their optical properties. The electronic absorption and emission of the macromolecules in solution were evaluated; and the results indicated no meaningful ground-state and excited singlet state intramolecular charge transfer interactions. However, the laser flash photolysis results could be explained in terms of the electron transfer quenching of the excited triplet methanofullerene moiety by the center metal–ligand complex in the macromolecules. The optical limiting properties of the macromolecules in solution were also investigated in comparison with those of the ligands for an evaluation of the complexation effects. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Terpyridine; Metal–ligand complex; Fullerene photophysics; Optical limiting; Photoinduced electron transfer

## 1. Introduction

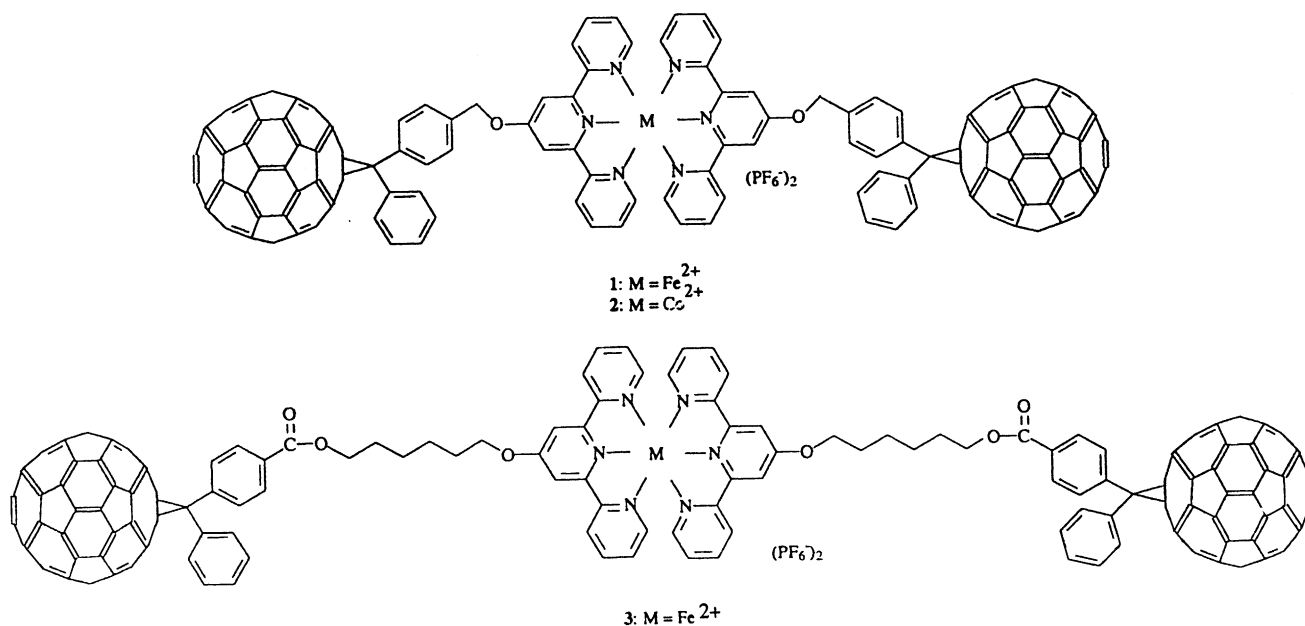
The complexation via coordinating 2,2':6',2''-terpyridine with metal ions serves as a convenient and specific linkage for dimeric and other macromolecules [1–27]. These metal–ligand complexes have interesting electrochemical and photoelectrochemical properties; and the properties are dependent on the selection of metal ions [25–27]. For example, the Ru(II)–terpyridine complex, similar to its Ru(II)–bipyridine counterpart, exhibits electron donating abilities, amenable to use as electron donor in redox dyads [27]. On the other hand, fullerene C<sub>60</sub> is an excellent electron acceptor [28–34], commonly serving as the electron accepting moiety in fullerene-based redox molecules. Optical spectroscopic techniques are widely used in the study of the ground-state and photoinduced redox activities of these molecules. However, while redox dyads containing a C<sub>60</sub> cage have been reported, the use of terpyridine in such

complexes has been scarce [35–40]. One noticeable work was reported by Diederich and coworkers for coupling methano-C<sub>60</sub> derivatives with a Ru(II)–terpyridine complex [35]. The synthesis normally requires elevated temperature to achieve full complexation to the Ru(II) ion. These kinds of fullerene-based macromolecules generally have poor solubility due to the contradictory solvation properties of the metal–ligand complex and the fullerene cage, which contribute to the difficulties with the synthesis and characterization of these macromolecules [37,38]. For dimeric fullerene macromolecules in particular, there have been no reports on the use of metalterpyridine complexes as linkages for the dimerization, according to an exhaustive literature search. In fact, for the linking of two fullerene cages via Pt–amine complexation, each cage with the ligand was penta-functionalized for necessary solubility improvements [41].

Here we report the synthetic preparation of metal-centered dimeric fullerene macromolecules **1**, **2** and **3** via the complexation of two fullerenedylated 2,2':6',2''-terpyridine ligands with a metal ion. These macromolecules are soluble in some organic solvents, which have allowed their structural characterization and an evaluation of their ground-state and excited-state properties using optical spectroscopic methods.

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## 2. Experimental

### 2.1. Materials

Fullerene-C<sub>60</sub> (99%) was obtained from BuckyUSA. 4'-Hydroxy-2,2':6',2''-terpyridine, commercially available from Aldrich, was prepared according to the literature procedure [42]. Reagent grade solvents were dried and distilled before use. Silica gel for column chromatography was obtained from ASA Scientific Adsorbents. Deuterated solvents for NMR experiments were obtained from Cambridge Isotope Laboratories.

### 2.2. 4-Bromomethylbenzophenone (**4**)

4-Methylbenzophenone (4 g, 20.4 mmol) was dissolved in carbon tetrachloride (200 ml) in a round-bottomed flask. After NBS (3.8 g, 21.3 mmol) was added, the solution was irradiated by a 100 W halogen lamp at 40 °C for 1 h. Upon filtering to remove solids, the solution was twice washed with water, dried with magnesium sulfate, and then evaporated to remove the solvent. The pale yellow solid thus obtained was recrystallized in carbon tetrachloride for purified **4** (~70% overall yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.54 (s, 2H, CH<sub>2</sub>Br), 7.48 (m, 4H, ArH), 7.60 (m, 1H, ArH), 7.79 (m, 4H, ArH) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 32.51 (CBr), 128.58, 129.17, 130.24, 130.78, 132.80, 137.67, 142.32, 196.21 (C=O) ppm.

### 2.3. 4-(2,2':6',2''-Terpyridyl-4'-oxy)methylbenzophenone (**5**)

4'-Hydroxy-2,2':6',2''-terpyridine (3 g, 10.9 mmol) was dissolved in acetonitrile (100 ml) in a round-bottomed flask.

To the solution was added potassium carbonate (12.04 g, 87.2 mmol) and catalytic amount of potassium iodide. The mixture was refluxed for 2 h, followed by the addition of **4** (3.64 g, 13.2 mmol), and then refluxed again overnight. Upon removing solids via filtration, the solution was evaporated to obtain the reaction mixture. The separation of the mixture using column chromatography (chloroform/acetone: 10/1) afforded 4.7 g **5** (~85% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 5.35 (s, 2H, CH<sub>2</sub>), 7.30 (m, 2H), 7.48 (t, 2H, *J* = 7.5 Hz), 7.55 (m, 3H), 7.79–7.84 (m, 6H), 8.12 (s, 2H), 8.61 (d, 2H, *J* = 7.5 Hz), 8.67 (d, 2H, *J* = 7.5 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 69.26 (CH<sub>2</sub>-OAr), 107.59, 121.44, 124.04, 127.03, 128.42, 130.13, 130.52, 132.58, 136.92, 137.30, 137.57, 140.83, 149.15, 155.94, 157.34, 166.71, 196.34 (C=O) ppm.

### 2.4. 4-(2,2':6',2''-Terpyridyl-4'-oxy)methylbenzophenone hydrazone (**6**)

A solution of **5** (2.37 g, 5.34 mmol) and hydrazine (1.7 g, 53.4 mmol) in ethanol (50 ml) was refluxed in a round-bottomed flask for 60 h. The reaction mixture was then concentrated to a small volume and cooled down to produce white solids. The recrystallization in ethanol afforded 1.79 g **6** (~73% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 5.31 and 5.40 (s, <sup>1</sup>H, NH<sub>2</sub>), 5.45 (s, 2H, CH<sub>2</sub>), 7.26–7.58 (m, 10H), 7.67 (d, 2H, *J* = 8.5 Hz), 7.85–7.90 (m, 2H), 8.12 and 8.65 (s, 2H), 8.63 and 8.65 (d, 2H, *J* = 7.5 Hz), 8.70 and 8.71 (m, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 69.65, 69.78 (CH<sub>2</sub>), 107.69, 121.47, 124.02, 126.56, 126.74, 127.62, 128.24, 128.26, 128.50, 129.31, 129.42, 132.94, 136.94, 136.96, 149.17, 156.00, 157.44, 166.70 ppm.

### 2.5. 4-[(2,2':6',2''-Terpyridyl-4'-oxy)methyl]phenylphenyldiazomethane (7)

To the solution of **6** (200 mg, 0.456 mmol) in dichloromethane (100 ml) was added HgO; and the mixture was stirred at room temperature for 2 days. Upon filtration, the purple solution was evaporated to yield a red-colored oil, which was used without further purification. FT-IR: 3055.3, 2042.6 (C=N<sup>+</sup>=N<sup>-</sup>), 1659.6, 1574.5, 1412.8, 1353.2, 1191.5, 1097.9, 1021.3, 800.0, 748.9, 697.9, 655.3 cm<sup>-1</sup>.

### 2.6. 6-(2,2':6',2''-Terpyridin-4'-yl)oxyhexanol (8)

4'-Hydroxy-2,2':6',2''-terpyridine (498 mg, 0.2 mmol) was dissolved in THF (50 ml) in a round-bottomed flask. Sodium hydride (240 mg, 60%, 6 mmol) was added. The mixture was stirred for 30 min, added with excess amount of 6-chlorohexanol (546 mg, 0.46 ml), and then refluxed overnight. After water was added carefully, the mixture was extracted twice with diethyl ether. The diethyl ether solution thus obtained was thoroughly washed with aqueous sodium carbonate and water, dried with sodium sulfate, and then evaporated to remove the solvent to obtain **8** as a white solid (~85% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.58–1.67 (m, 4H), 1.83–1.92 (m, 4H), 3.68 (t, 2H, *J* = 6.4 Hz), 4.25 (t, 2H, *J* = 6.4 Hz), 7.32–7.37 (qd, 2H, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 4.6 Hz, *J*<sub>3</sub> = 1.2 Hz), 7.86 (td, 2H, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.8 Hz), 8.02 (s, 2H), 8.62 (dd, 2H, *J*<sub>1</sub> = 7.9 Hz, *J*<sub>2</sub> = 0.7 Hz), 8.70 (dt, 2H, *J*<sub>1</sub> = 7.0 Hz, *J*<sub>2</sub> = 2.2 Hz, *J*<sub>3</sub> = 1.0 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 25.69, 26.03, 29.10, 32.94, 63.13, 68.44, 107.87, 121.75, 124.12, 137.28, 149.12, 156.24, 157.09, 167.67 ppm.

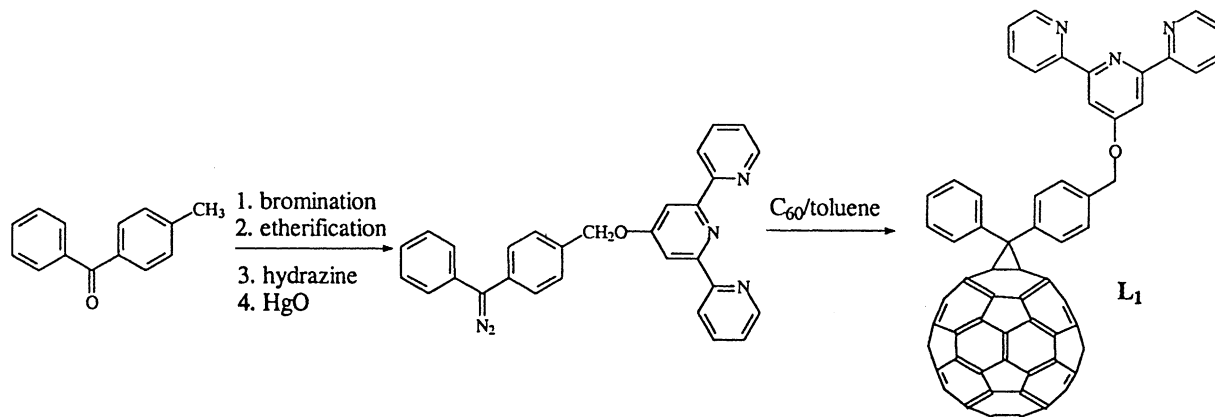
### 2.7. 6-[(2,2':6',2''-Terpyridin-4'-yl)oxy]hexyl-4-benzoylbenzoate (9)

4-Benzoyl benzoic acid (253 mg, 1.12 mmol) and pyridine (0.12 ml) were mixed in a small round-bottomed flask.

After the dropwise addition of thionyl chloride (0.9 ml), the mixture was stirred under nitrogen protection for 1 h. To the mixture was then added through a syringe a solution of **8** (349 mg, 1 mmol) in pyridine (0.236 ml) and dichloromethane (20 ml) also under nitrogen protection; and the resulting mixture was stirred overnight. After the evaporation of dichloromethane and excess thionyl chloride and the addition of water, the reaction mixture was extracted with diethyl ether twice. The diethyl ether solution thus obtained was washed with aqueous sodium carbonate and water, and dried with magnesium sulfate. Concentrating the solution and recrystallization afforded **9** as a white solid (80% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.40–1.60 (bs, 4H), 1.77–1.83 (m, 4H), 4.17 (t, 2H, *J* = 6.4 Hz), 4.32 (t, 2H, *J* = 6.4 Hz), 7.24 (m, 2H), 7.42 (t, 2H, *J* = 7.8 Hz), 7.52 (t, 1H, *J* = 7.4 Hz), 7.72–7.77 (m, 6H), 7.95 (s, 2H), 8.09 (d, 2H, *J* = 8.7 Hz), 8.55 (d, 2H, *J* = 7.8 Hz), 8.62 (d, 2H, *J* = 4.0 Hz) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 25.79, 25.85, 28.72, 28.97, 65.44, 68.02, 107.40, 121.38, 123.88, 128.49, 129.52, 129.81, 130.14, 133.95, 132.97, 136.84, 136.97, 149.04, 156.11, 157.05, 165.87, 167.28, 195.99 ppm.

### 2.8. 1-Phenyl-1-{1'-{4'-{6-[(2,2':6',2''-terpyridin-4'-yl)oxy]}hexyl}benzoate}methanotosylhydrazone (10)

A solution of **9** (222 mg, 0.39 mmol) and *p*-toluenesulfonyl hydrazide (79.8 mg, 0.43 mmol) in anhydrous ethanol (2 ml) was refluxed for 12 h, followed by the evaporation of the solvent. The reaction mixture was washed with cold diethyl ether to obtain the product **10** (70% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.50–1.55 (m, 4H), 1.80–1.90 (m, 4H), 2.31 and 2.39 (s, 3H), 4.23–4.26 (m, 4H), 7.10–7.48 (m, 11H), 7.81–8.15 (m, 8H), 8.60–8.70 (m, 4H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.87, 25.55, 25.95, 28.92, 29.13, 65.08, 65.34, 68.58, 108.14, 122.05, 124.39, 126.54, 126.87, 127.66, 128.17, 128.47, 128.76, 129.67, 129.97, 130.16, 130.83, 131.01, 135.85, 137.92, 145.60, 148.62, 153.55, 155.45, 156.40, 167.78 ppm.



2.9. 4'-[(2',2'':6'',2'''Terpyridyl-4''-oxy)methyl]phenylphenyl 1,2-methano[60]fullerene (**L**<sub>1</sub>)

To a solution of C<sub>60</sub> (336 mg, 0.47 mmol) in toluene (170 ml) was added **7** (251 mg, 0.55 mmol) under nitrogen protection. After the reaction at room temperature for 12 h, the solution was refluxed for 48 h. The separation using column chromatography afforded 270 mg **L**<sub>1</sub> as a brownish solid (50% yield based on the consumed C<sub>60</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 5.43 (s, 2H, CH<sub>2</sub>), 7.32 (m, 2H), 7.34 (t, <sup>1</sup>H, *J* = 7.8 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 7.62 (d, 2H, *J* = 7.8 Hz), 7.85 (dd, 2H, *J*<sub>1</sub> = 7.75 Hz, *J*<sub>2</sub> = 1.8 Hz), 8.16 (m, 6H), 8.63 (d, 2H, *J* = 8.2 Hz), 8.69 (d, 2H, *J* = 5.0 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 58.12, 69.77, 79.07, 107.81, 121.58, 124.10, 128.01, 128.42, 129.04, 131.16, 131.40, 136.25, 137.01, 138.32, 138.36, 139.07, 139.16, 141.07, 142.30, 142.32, 142.44, 143.17, 144.01, 144.44, 144.81, 144.89, 145.28, 145.36, 145.54, 148.29, 149.27, 156.19, 157.45, 167.03 ppm [43–45].

2.10. 61-Phenyl-61-{4'-{6-[(2,2':6',2''-terpyridin-4'-yl)oxy]}hexyl}benzoate 1,2-dihydro-1,2-methano[60]fullerene (**L**<sub>2</sub>)

C<sub>60</sub> (218 mg, 0.2 mmol), **10** (121 mg, 0.17 mmol), sodium hydride (175 mg, 60%, 4.4 mmol) were added to degassed 1,2-dichlorobenzene (50 ml) in a round-bottomed flask. The mixture was stirred at 85 °C under nitrogen protection for 8 h. After carefully adding water to quench the reaction, the organic layer was separated, washed with water, dried and then concentrated. The separation using column chromatography (chloroform/acetone: 5/1) yielded a brownish solid, which was then refluxed in toluene for 24 h to afford **L**<sub>2</sub> (35% yield based on the consumed C<sub>60</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.54 (s, 4H), 1.75 (t, 2H, *J* = 6.4 Hz), 1.82 (t, 2H, *J* = 6.4 Hz), 4.17 (t, 2H, *J* = 6.4 Hz), 4.28 (t, 2H, *J* = 6.4 Hz), 7.23–7.27 (m, 2H), 7.32 (t, 1H, *J* = 7.4 Hz), 7.41 (t, 2H, *J* = 7.4 Hz), 7.77 (td, 2H, *J*<sub>1</sub> = 1.8 Hz, *J*<sub>2</sub> = 7.8 Hz), 7.94 (s, 2H), 8.01 (d, 2H, *J* = 7.0 Hz), 8.11 (dd, 4H, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 3.7 Hz), 8.54 (d, 2H, *J* = 7.8 Hz), 8.61 (d, 2H, *J* = 4.1 Hz) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 25.84, 25.97, 28.81, 29.02, 57.69 (methano-C), 65.24, 68.09, 78.59, 107.48, 121.47, 123.90, 128.32, 128.99, 130.19, 130.21, 131.07, 136.90, 138.11, 138.26, 138.37, 140.98, 141.02, 142.18, 142.24, 142.29, 143.01, 143.08, 143.17, 144.89, 144.37, 144.38, 144.65, 144.68, 144.74, 144.79, 145.19, 145.26, 145.33, 147.81, 147.91, 149.10, 156.24, 157.13, 166.23, 167.37 ppm [43–45].

2.11. Fe(**L**<sub>1</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (**1**)

To a solution of **L**<sub>1</sub> (50 mg) in chloroform/ethanol mixture (2:1, 50 ml) was added an excess amount of KPF<sub>6</sub> and then an aqueous Fe(NH<sub>4</sub>SO<sub>4</sub>)<sub>2</sub> solution. The mixture was stirred for 5 min, followed by dropwise addition of ethanol until no visible water droplets. The reaction mixture was filtered;

and the solid portion was washed thoroughly with water, ethanol, and chloroform to obtain the dark purple colored complex **1** (65% yield). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 5.54 (s), 6.95 (t, *J* = 6.9 Hz), 7.02 (d, *J* = 5.1 Hz), 7.23 (t, *J* = 7.4 Hz), 7.35 (t, *J* = 7.8 Hz), 7.65 (d, *J* = 7.8 Hz), 7.76 (t, *J* = 7.3 Hz), 8.23 (d, *J* = 7.3 Hz), 8.37 (d, *J* = 8.3 Hz), 8.57 (d, *J* = 7.8 Hz), 8.86 (s) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ = 58.56, 67.59, 79.72, 112.39, 128.09, 129.39, 129.65, 131.74, 132.09, 137.59, 137.75, 140.70, 142.22, 142.27, 142.92, 142.98, 143.06, 143.93, 143.95, 144.31, 144.34, 144.64, 144.71, 145.19, 145.29, 146.32, 146.44, 149.34, 149.43, 158.39, 160.89 ppm.

2.12. Co(**L**<sub>1</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (**2**)

The synthesis is the same as that for **1**, except for the use of anhydrous CoCl<sub>2</sub> instead of Fe(NH<sub>4</sub>SO<sub>4</sub>)<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 7.41, 7.59, 7.97, 8.22, 8.89, 9.50, 10.02, 10.66, 12.33 ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ = 65.47, 80.75, 129.60, 129.99, 130.17, 131.23, 132.72, 133.09, 133.45, 133.83, 134.13, 134.74, 138.33, 138.52, 140.07, 140.61, 141.12, 142.43, 142.59, 142.71, 143.26, 143.35, 144.23, 144.68, 144.83, 144.89, 144.99, 145.36, 145.44, 146.94, 147.11, 150.05, 150.45, 156.57 ppm.

2.13. Fe(**L**<sub>2</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (**3**)

To a solution of **L**<sub>2</sub> (63 mg, 0.05 mmol) in chloroform/ethanol mixture (3:1) was added FeCl<sub>2</sub>·4H<sub>2</sub>O (5 mg, 0.0025 mmol). The mixture was stirred at room temperature under nitrogen protection for 20 min, followed by the addition of an excess amount of KPF<sub>6</sub>. The precipitate was filtered out and washed thoroughly with deionized water, chloroform, and cold ethanol to obtain the purple colored complex **3** (70% yield). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 1.65–1.71 (m, 8H), 1.82–1.88 (m, 4H), 2.07 (bs, 4H), 4.39 (bs, 4H), 4.62 (bs, 4H), 7.14 (bs, 4H), 7.20 (bs, 4H), 7.41 (t, 2H, *J* = 6.9 Hz), 7.53 (t, 4H, *J* = 6.5 Hz), 7.95 (bs), 8.12 (d, 4H, *J* = 7.3 Hz), 8.41 (d, 4H, *J* = 6.9 Hz), 8.58 (d, 4H, *J* = 7.4 Hz), 8.81 (d, 4H, *J* = 6.9 Hz), 8.93 (s, 4H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ = 25.88, 28.86, 28.99, 55.81, 58.21, 79.32, 82.34, 112.27, 127.84, 127.99, 128.23, 129.10, 129.33, 130.19, 131.60, 132.07, 132.38, 132.63, 132.68, 132.97, 137.39, 137.86, 138.64, 138.95, 140.44, 140.60, 142.13, 142.19, 142.21, 142.88, 142.98, 143.00, 144.27, 144.6–144.8, 145.19, 145.23, 145.33, 145.74, 146.23, 149.00, 158.47, 160.82, 165.19 ppm.

2.14. Measurements

NMR spectra were recorded on a Bruker AC-300 NMR spectrometer and a Jeol Eclipse +500 NMR spectrometer. FT-IR measurements were carried out using a Nicolet Magna-IR 550 FT-IR spectrometer.

### 2.15. Absorption and emission

UV/Vis absorption spectra were obtained using a Shimadzu UV2101-PC spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator, and two detectors to cover the visible and near IR wavelength regions. Unless specified otherwise, fluorescence spectra were corrected for nonlinear instrumental response by the use of predetermined correction factors. Fluorescence decays were measured using the time-correlated single photon counting (TCSPC) method [46].

### 2.16. Transient absorption

Transient absorption spectra were obtained using a laser flash photolysis setup. The excitation source was the third harmonic of a Continuum Surelite-IQ-switched Nd:YAG laser. Excitation energies were kept low (a few mJ) to minimize photodegradation. A Perkin Elmer xenon flash lamp was used as the probing light source; and the microsecond light pulses were focused into a fiber optic cable. The output from the optic fiber was collimated, passed through the sample cuvette, and refocused into a second fiber optic cable, which was attached to an Ocean Optics SD2000 spectrometer with a CCD detector. The synchronization of the laser, probing flash lamp, and detector was achieved using a BNC mode 500 pulse generator. All transient absorption spectra were integrated over a time period corresponding to the pulse width of the flash lamp. The sample solutions were carefully purged with argon for 5 min before each spectrum was taken; and further argon purging showed no increase in the transient absorption signal. The spectra were collected at 10 Hz and averaged over  $\sim 100$  laser shots.

### 2.17. Optical limiting

The setup for optical limiting measurements (Fig. 1) consisted of a Continuum Surelite-I Q-switched Nd:YAG laser operated in the single shot mode. The infrared fundamental was frequency doubled to generate the second harmonic at 532 nm, with the maximum energy of 160 mJ/pulse (FWHM  $\sim 5$  ns). The pulse energy was varied from 10 to 160 mJ/pulse by using a waveplate–polarizer combination. Unless specified otherwise, the laser output was collimated; and all optical limiting measurements were carried out using the collimated laser beam. The beam diameter was determined in individual measurements for calculating the energy density (generally  $\sim 6$  mm, corresponding to energy densities in the range  $0.035$ – $0.57$  J/cm<sup>2</sup>). For higher energy densities, the laser beam diameter was reduced in half by using a Galilean style telescope consisting of a plano-concave lens and a plano-convex lens. The detector was a Scientech Mentor MC2501 calorimeter controlled by a Scientech MD10 meter.

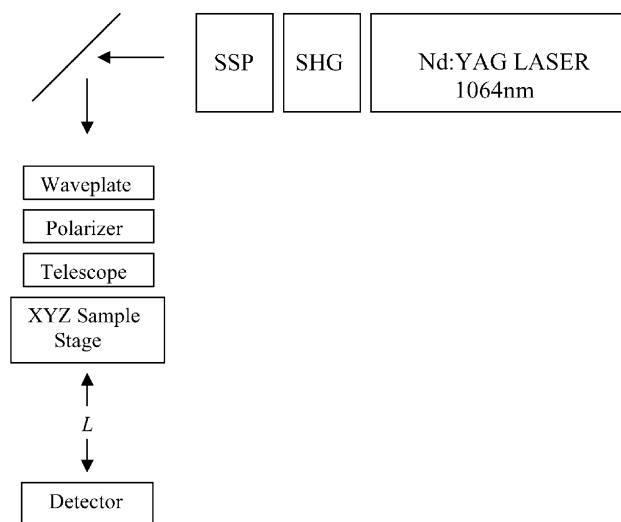


Fig. 1. Experimental setup for optical limiting measurements.

## 3. Results and discussion

### 3.1. Synthesis of the macromolecules

The diazo addition method, developed by Wudl et al. [43–45,47–50] is often used to synthesize fulleroids ([5,6]-open) and methanofullerenes ([6,6]-closed). The stable diazo compounds are typically prepared from benzophenone derivatives via hydrazine reduction to form hydrazone, followed by oxidation. The appearance of an IR absorption at  $\sim 2040$  cm<sup>-1</sup> in the FT-IR spectrum indicates the formation of the diazo precursor. The derivatization of benzophenone with a relatively large terpyridyloxymethyl group (**5**) apparently has little effect on the preparation of the hydrazone (**6**) and the subsequent oxidative conversion to the diazo compound (**7**). The reaction yields are, in general, similar to those for the parent benzophenone [47–50].

The diazo addition to the fullerene cage produces a mixture of [5,6]-open (fulleroid) and [6,6]-closed (methanofullerene) monoadducts [47–50]. Since the latter is thermodynamically more stable, the fulleroid may be converted to methanofullerene either thermally or photochemically [47–50]. In the preparation of **L**<sub>1</sub>, a complete conversion to the methanofullerene was achieved via refluxing the reaction mixture in toluene for 2 days. The conversion is apparently more efficient than that for the adducts corresponding to the parent benzophenone, where the conversion from [5,6]-open to [6,6]-closed is so inefficient that it requires photoirradiation to improve efficiency [47–51]. However, the conversion reaction for **L**<sub>1</sub> is still much less efficient than that for the adducts with electron donor-substituted phenyl groups [51].

Among metal terpyridine complexes, the one with Fe(II) as the center metal is relatively easier to prepare at ambient temperature [52]. However, due to the opposite solubility



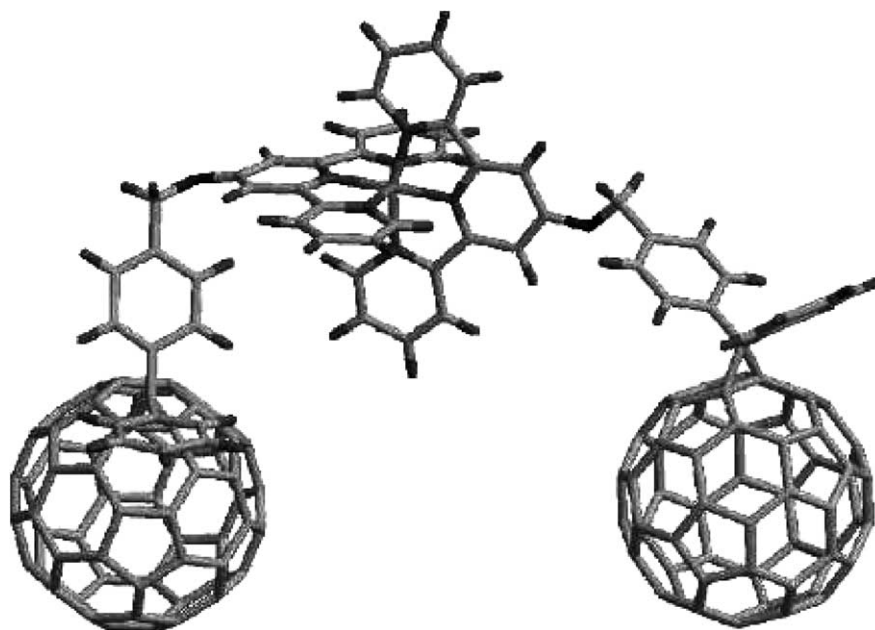


Fig. 2. Structure of **1** optimized using the MM<sup>+</sup> force field in the commercial software HYPERCHEM.

requirement of the complex from that of C<sub>60</sub>, the common procedure reported in the literature fails to yield the dimerization product. Instead, the reaction always produces a brown precipitate that is insoluble in common organic solvents. The addition of KPF<sub>6</sub> prior to the reaction and the use of an ethanol–chloroform mixture apparently promote the complexation reaction, yielding compound **1** as a dark purple precipitate. Although the compound **1** is insoluble in most organic solvents, it is reasonably soluble in DMSO, making it possible to use solution-based characterization techniques. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compound in DMSO-*d*<sub>6</sub> show signals that are consistent with the molecular structure of two fullerenedylated 2,2':6',2''-terpyridines binding with Fe(II) in an octahedral geometry. For a more visual representation of the macromolecule, the molecular structure was optimized in a computation using the MM<sup>+</sup> force field in the commercial software package HYPERCHEM.<sup>1</sup> A minimized structure thus calculated is shown in Fig. 2.

The same reaction conditions are applicable to the synthesis of the Co(II)-centered terpyridine-C<sub>60</sub> macromolecule **2**, with a comparable yield. The compound **2** is also insoluble in most organic solvents, but reasonably soluble in DMSO. However, the NMR characterization of this complex is much less quantitative because the signals are broadened and shifted due to the paramagnetic effect of Co(II).

A fullerenedylated terpyridine ligand of a longer alkyl spacer was designed for improved solubility characteristics of the resulting metal–ligand complex in common polar organic solvents such as acetone and acetonitrile. For the dimeric macromolecule **3**, the synthesis of the fullerenedylated terpyri-

dine of a six-carbon alkyl chain was somewhat more difficult than its counterpart of only a methylene spacer. The difficulties were, e.g., with the selection of an appropriate solvent system that would discriminate the hydrazone from the diazo compound and with the long oxidation time required for the hydrazone to diazo conversion. Thus, a strategy of in situ diazo formation and addition to fullerene was employed [53,54]. In the synthesis, the hydrazone was prepared using tosylhydrazide. Then, the diazo compound formed from the oxidation was used in situ in the addition to fullerene. The yield with the one-step procedure was similar to that with the traditional diazo addition reaction with fullerene.

The Fe(II)-centered dimeric fullerene macromolecule **3** does have better solubility characteristics over its shorter-spacer counterpart **1**. The compound **3** is somewhat soluble in room-temperature acetone and acetonitrile, in addition to being soluble in DMSO.

### 3.2. Absorption and emission

The metal-centered dimeric fullerene macromolecules are strongly absorptive in the visible, due primarily to the absorption of the metal–terpyridine complex. However, there are apparently no meaningful ground-state charge transfer interactions between the metal–terpyridine complex and the fullerene cages. For example, the absorption spectrum of **1** can be produced nearly quantitatively by superposing the spectra of L<sub>1</sub> and the model Fe(II)–terpyridine complex (Fig. 3).

The Fe(II)–terpyridine complex is non-luminescent due primarily to the short excited state lifetime [55]. Similarly, there is no luminescence when **1** is photoexcited

<sup>1</sup> The software package HYPERCHEM is a product of Hypercube, Inc.

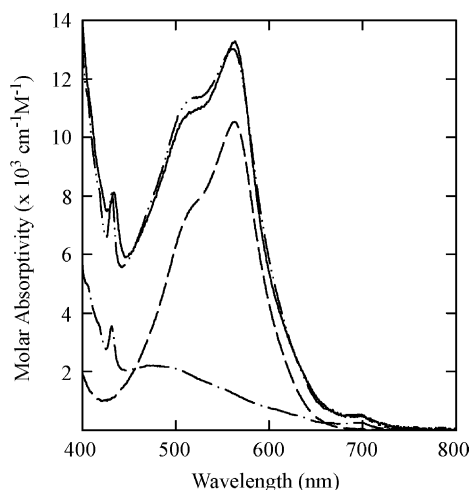


Fig. 3. The absorption spectrum of **1** in room-temperature DMSO (—) is compared with the constructed spectrum (—·—) that is equal to the spectrum of model Fe(II)-terpyridine complex (---) plus  $2 \times$  the spectrum of **L**<sub>1</sub> (- - -).

at wavelengths where the absorption is dominated by the metal-terpyridine complex moiety in the macromolecule. When the photoexcitation is at wavelengths where both the Fe(II)-terpyridine complex and the methanofullerene cage absorb, weak fluorescence from the latter can be observed. However, the methanofullerene fluorescence parameters are not affected by the presence of the metal-terpyridine complex moiety in the macromolecule beyond the ground-state absorption “inner-filter effect” on the observed fluorescence yield. For the Co(II)-centered macromolecule **2**, the photo-physical properties (Fig. 4) are essentially the same as those of the macromolecule **1**. Thus, there is no evidence for any meaningful energy/charge transfer interactions between the excited singlet methanofullerene moiety and the center

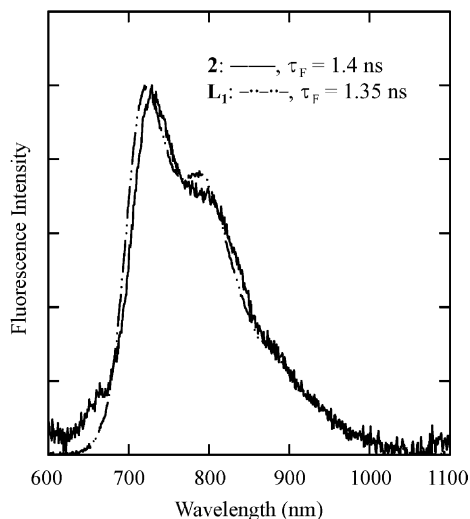


Fig. 4. The fluorescence spectrum and lifetime of **2** in room-temperature DMSO are compared with those of **L**<sub>1</sub>.

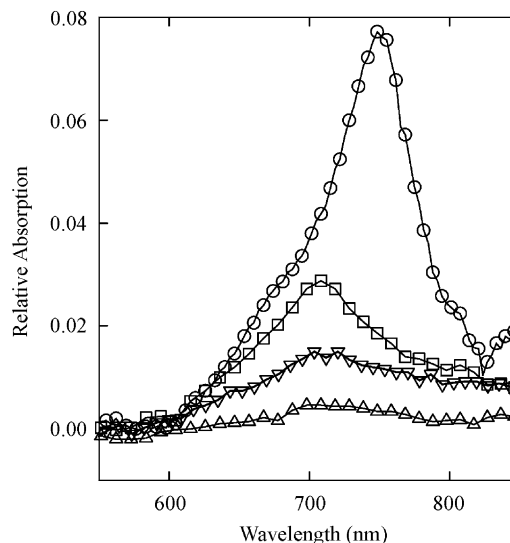


Fig. 5. Triplet-triplet absorption spectra of **1** in room-temperature DMSO ( $\Delta$ ) and DMSO-pyridine mixture ( $\nabla$ ) are compared with those of the ligand **L**<sub>1</sub> in chloroform ( $\square$ ) and C<sub>60</sub> in toluene ( $\circ$ ) with matched optical densities at the laser excitation wavelength of 355 nm.

metal-terpyridine complex in the macromolecules. Since these macromolecules can be considered as redox dyads, with the center metal-terpyridine complex as electron donor and the photoexcited methanofullerene moiety as electron acceptor (see below), the lack of fluorescence quenching via electron transfer interactions may be attributed to the short excited singlet state lifetimes. However, the electron transfer quenching likely becomes significant for the excited triplet methanofullerene moiety, as revealed by the transient absorption results.

### 3.3. Transient absorption

The triplet transient absorption spectrum of C<sub>60</sub> in toluene was recorded for the purpose of calibration. The spectrum (Fig. 5) is in excellent agreement with the literature results [56]. For **L**<sub>1</sub>, the transient absorption measurement was carried out in a chloroform solution. As compared in Fig. 5, the transient absorption spectrum of **L**<sub>1</sub> is broad and structureless, with the absorption peak blue-shifted  $\sim 40$  nm from that of C<sub>60</sub> and weaker in intensity. The result is, in general, agreement with those of methano-C<sub>60</sub> derivatives reported in the literature [56,57].

The transient absorption of the macromolecule **1** in a DMSO solution was measured under the same conditions as those for C<sub>60</sub> and **L**<sub>1</sub>. However, the observed spectrum is significantly weaker than that of **L**<sub>1</sub>. Since the excited states of Fe(terpyridine)<sub>2</sub><sup>2+</sup> complexes are known to have lifetimes on the nanosecond time scale [55], the transient absorption of macromolecule **1** is most likely due to the triplet states of the methanofullerene moiety, similar to those in **L**<sub>1</sub>. Thus, the apparently weaker transient absorption may be attributed in part to the ground-state absorption by the

Fe(II)–terpyridine complex moiety in the macromolecule, which serves as an “inner filter” for the absorption of the methanofullerene moiety at the laser excitation wavelength 355 nm. As shown in Fig. 3, the relative absorption contributions of the Fe(II)–terpyridine and methanofullerene moieties are about 1:2 at 355 nm, so that the ground-state absorption inner-filter effect cannot fully account for the observed large reduction in transient absorption from  $L_1$  to the macromolecule **1**. Instead, there must be another dominating mechanism for the significant quenching of the excited triplet methanofullerene moiety in **1**.

One strong possibility for the quenching is electron transfer from the excited triplet methanofullerene moiety to the center Fe(II)–terpyridine complex. In macromolecules, electron transfer processes are typically interpreted in terms of the classical Marcus theory, which correlates the electron transfer rate constant with the Gibbs free energy  $\Delta G_{ET}$  (electron transfer driving force) [58–60]. According to Rehm and Weller [60], generally the maximum electron transfer rate is achieved at the driving force  $\Delta G_{ET}$  of about  $-5$  kcal/mol. By using the same equation due to Rehm and Weller, a  $\Delta G_{ET}$  value of close to  $-5$  kcal/mol can be estimated for the redox pair (the Fe(II)–terpyridine complex as donor and the excited triplet methanofullerene as acceptor) in the macromolecule **1** [61]. The result is consistent with the fact that Fe(terpyridine) $_2^{2+}$  readily undergoes reversible single electron oxidation [62] and the excited fullerene is an excellent electron acceptor [28–34]. However, a verification of the electron transfer quenching mechanism in the macromolecule **1** has been unsuccessful, with failed attempts for detecting the fullerene anion radical absorption in the near IR [33,34]. It is possible that the radical ion pair generated in the electron transfer undergoes efficient intramolecular recombination on a timescale shorter than the limit of our laser flash photolysis setup.

The quenching of the transient absorption is significantly less in the presence of pyridine. As compared in Fig. 5, the transient absorption of **1** in a DMSO–pyridine mixture is only slightly weaker than that of the ligand  $L_1$ . Similar effect on photoinduced electron transfer in metal–ligand complex-based dyads due to the presence of pyridine or piperidine can be found in the literature [63]. However, the mechanistic details for the effect of pyridine on the intramolecular electron transfer quenching in **1** remain to be explored in further investigations.

### 3.4. Optical limiting

It is well established that fullerene  $C_{60}$  in solution is an excellent optical limiter [64–66]. For the purpose of calibrating the setup in Fig. 1, optical limiting responses of  $C_{60}$  in toluene solution were determined (Fig. 6), with the results agreeing well with those reported in the literature [64–66]. For the ligand  $L_1$  in chloroform, the optical limiting responses are slightly weaker than those of the parent  $C_{60}$  (Fig. 6), consistent with the results of methanofullerene

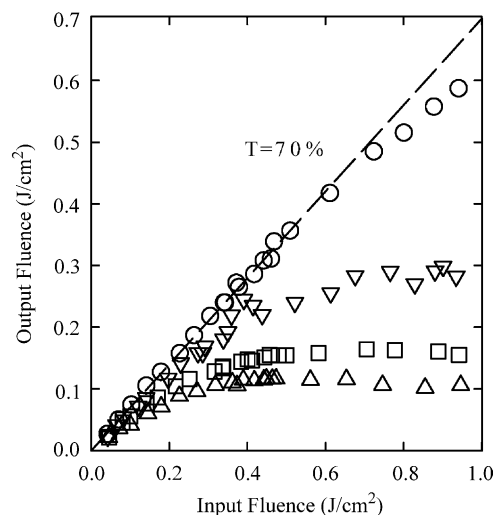


Fig. 6. Optical Limiting responses (5 ns laser pulses at 532 nm) of **1** in room-temperature DMSO (○) and DMSO–pyridine mixture (△) are compared with those of the ligand  $L_1$  in chloroform (□) and  $C_{60}$  in toluene (△) at 70% linear transmittance.

derivatives in general [65–69]. However, upon the complexation with a center metal, the dimeric fullerene macromolecules thus formed hardly limit the laser pulses. As shown in Fig. 6, the output fluences from the **1** solution in DMSO follow closely the linear transmittance line with respect to the input fluences, except for a small deviation at high fluence values. Since the Fe(II)–terpyridine complex moiety contributes significantly to the overall ground-state absorption of the macromolecule at 532 nm, the lack of optical limiting of **1** in solution indicates that the center complex not only contributes no optical limiting, but also serves as an “inner filter” to hinder the optical limiting of the methanofullerene moiety (strong ground-state absorption of the complex damaging the reverse saturable absorption conditions with the methanofullerene). In addition, the center complex likely quenches the excited triplet methanofullerene moiety via electron transfer, which further reduces the optical limiting responses of the macromolecule. This electron transfer effect is made evident by the optical limiting results of **1** in a DMSO–pyridine mixture. Due to the presence of pyridine, which apparently suppresses the electron transfer process, the optical limiting responses of **1** are considerably improved (Fig. 6).

## 4. Summary

Dimeric fullerene macromolecules can be obtained via the complexation of two fullerenedylated 2,2':6',2''-terpyridine ligands with a metal ion. The solubility, though limited, is valuable to the investigation of these macromolecules. The complexation has significant effects on the optical properties of the individual ligands. These macromolecules are structurally characteristic of redox dyads; but photoinduced



electron transfer interactions are hindered by the short excited state lifetimes, except perhaps for the excited triplet state of the methanofullerene moiety. Further investigations are focused on a verification of the electron transfer interactions and a determination of the single-crystal structure for these macromolecules.

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