

研究论文

**C60吡咯烷羧酸衍生物的合成及其在水溶液中的聚集行为**

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**摘要** C60与亚氨基二乙酸甲酯[NH(CH<sub>2</sub>COOMe)<sub>2</sub>]的光化学反应制得2,5-双(甲氧羰基)富勒烯吡咯烷(**1**), 产率为52% (基于已反应的C60). C60吡咯烷衍生物**1**与氯乙酸甲酯(CICH<sub>2</sub>COOCH<sub>3</sub>)的*N*-烷基化反应, 在微波辐射、无溶剂及相转移条件下, 得到2,5-双(甲氧羰基)-*N*-(甲氧羰基)甲基富勒烯吡咯烷(**2**), 产率47%(基于C60吡咯烷衍生物**1**). C60吡咯烷衍生物**1**和**2**用NaH, CH<sub>3</sub>OH水解后, 经盐酸酸化得相应的二羧酸衍生物**3**和三羧酸衍生物**4**, 产率分别为65%和53% (基于C60吡咯烷衍生物**1**和**2**). C60吡咯烷衍生物**1**~**4**的结构由<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, FAB-MS和元素分析证实. 用电导法测定了C60吡咯烷二羧酸**3**和三羧酸**4**钠盐的临界聚集浓度(CAC), 分别为3.58×10<sup>-4</sup> mol/L (**3**)和3.33×10<sup>-4</sup> mol/L (**4**). 这一结果被C60吡咯烷衍生物**3**和**4**, 在临界聚集浓度(CAC)附近的UV-Vis光谱的特征变化所支持. 透射电子显微镜(TEM)和静态光散射(SLS)等方法也被用于检测C60吡咯烷衍生物**3**和**4**在临界聚集浓度(CAC)时的聚集行为, 结果显示, C60吡咯烷衍生物**3**在缓冲溶液中(0.001 mol/L NaCO<sub>3</sub>-NaHCO<sub>3</sub>), 其聚集体粒径的大小(*R<sub>g</sub>* ≈ 21 nm)不同于C60吡咯烷衍生物**4** (*R<sub>g</sub>* ≈ 23 nm). C60吡咯烷二羧酸**3**钠盐的临界聚集浓度(CAC)比C60吡咯烷三羧酸**4**钠盐的临界聚集浓度(CAC)大, 聚集体粒径大小的不同, 表明C60单加成衍生物加成基团中羧基(COOH)数目的多少对其聚集行为的影响. 用化学发光法分别检测了C60吡咯烷二羧酸**3**和C60吡咯烷三羧酸**4**在缓冲溶液(0.05 mol/L NaCO<sub>3</sub>-NaHCO<sub>3</sub>)

中对邻苯三酚自氧化产生的超氧阴离子(O<sub>2</sub><sup>-</sup>)的清除活性. C60衍生物**3**和**4**对 O<sub>2</sub><sup>-</sup>的清除呈现有明显的剂量效应, 但当超过一定浓度时(**3**: ~3.50×10<sup>-4</sup> mol/L, **4**: ~3.25×10<sup>-4</sup> mol/L), 清除效率出现转折, 并下降. 这一现象与电导率测定时出现的CAC现象相一致, 进一步证实了C60吡咯烷二羧酸**3**和C60吡咯烷三羧酸**4**在较高浓度的水溶液中有聚集的倾向, 也说明了C60吡咯烷二羧酸**3**和C60吡咯烷三羧酸**4**的聚集会影响其清除超氧阴离子(O<sub>2</sub><sup>-</sup>)的活性.

**关键词** [光化学反应](#) [微波辐射](#) [富勒烯吡咯烷衍生物](#) [临界聚集浓度](#) [静态光散射](#) [超氧阴离子自由基](#)  
分类号

**Synthesis of Fulleropyrrolidine Carboxylic Acids and Their Aggregation Behavior in Aqueous Solution**

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**Abstract** Photochemical reaction of C60 with iminodiacetic methyl ester [NH(CH<sub>2</sub>COOMe)<sub>2</sub>] produced 2,5-bis(methoxycarbonyl)fulleropyrrolidine (**1**) in a 52% yield (based on consumed C60). *N*-Alkylation of fulleropyrrolidine derivative **1** with methyl chloroacetate (CICH<sub>2</sub>COOCH<sub>3</sub>) by phase transfer catalysis without solvent under microwave irradiation afforded 2,5-bis(methoxycarbonyl)-*N*-(methoxycarbonyl)-methylfulleropyrrolidine (**2**) in a 47% yield (relative to the methyl derivative **1**). Fulleropyrrolidine derivatives **1** and **2** were hydrolyzed with NaH and methanol in toluene, and then acidified with HCl to result in the corresponding fulleropyrrolidine dicarboxylic acid (**3**) and fulleropyrrolidine tricarboxylic acid (**4**), respectively, in 65% and 53% yields (relative to fulleropyrrolidine derivatives **1** and **2**). Fulleropyrrolidine derivatives **1**~**4** were structurally characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, FAB-MS methods and elementary analysis. Critical aggregation concentrations (CAC) of sodium salts of dicarboxylic acid derivative **3** and tricarboxylic acid derivative **4** were determined by conductivity measurements, which were 3.58×10<sup>-4</sup> mol/L (**3**) and 3.33×10<sup>-4</sup> mol/L (**4**), respectively. The results were supported by characteristic change of UV-Vis absorption spectra of the derivatives **3** and **4** at the neighborhoods of CAC. The aggregation behavior of **3** and **4** was also examined using static light scattering (SLS) and transmission electron microscopic (TEM) techniques, and the aggregate sizes of derivative **3** (radius *R<sub>g</sub>* ~ 21 nm) in a buffer solution (0.001 mol/L Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>) were found to be different from derivative **4** (radius *R<sub>g</sub>* ~ 23 nm). Critical aggregation concentrations (CAC) of sodium salts of the derivative **3** is bigger than that of sodium salts of derivative **4**, and their aggregate sizes were different from each other, indicating that the formation of aggregate is effected by the number of carboxyl connected to fulleropyrrolidine mono-adduct derivatives. Scavenging

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effects of derivatives **3** and **4** on superoxide radicals ( $O_2^{\cdot-}$ ) in a buffer solution (0.05 mol/L  $Na_2CO_3$ - $NaHCO_3$ ) were studied by chemiluminescence technique. They were found to show an obvious quantity effect, that the eliminating efficiencies was increased with the increase of concentration. However, when exceeding certain concentration (CAC), the eliminating efficiency showed the turn (**3**:  $\sim 3.50 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , **4**:  $\sim 3.25 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ), and decline. This phenomenon was in accordance with that of CAC detected by conductance method, further confirming that derivatives **3** and **4** had tendency of aggregation in aqueous solution of higher concentration, and the formation of aggregate had a great influence on their scavenging activity for superoxide radicals ( $O_2^{\cdot-}$ ).

**Key words** [photochemical reaction](#) [microwave irradiation](#) [fulleropyrrolidine derivative](#) [critic aggregation concentration](#) [static light scattering](#) [superoxide radical](#)

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