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Self-assembly of the [60]fullerene-substituted oligopyridines on Au nanoparticles and the optical nonlinearities of the nanoparticles

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Abstract

The cycloaddition reaction of azido oligopyridine with [60]fullerene was used to synthesize two novel [60]fullerene derivatives containing bi/tri-pyridyl group, which were employed to self-assemble on the surface of gold nanoparticles. Optical nonlinearities of the gold nanoparticles in chloroform were determined by Z-scan technique and the optical limiting experiments with 532 nm, 8 ns and 40 ps duration laser pulses.

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1. Introduction

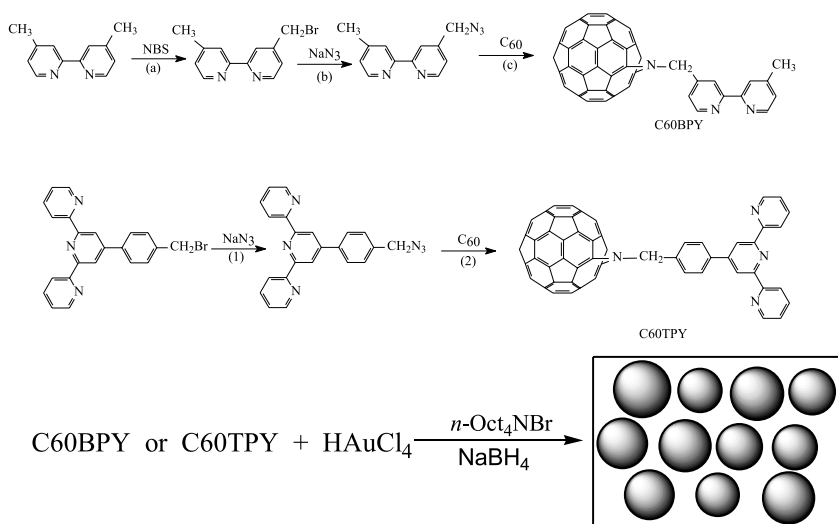
The self-assembly of fullerenes and fullerene derivatives onto a variety of surfaces of interest substrates such as metals, semiconductors, insulators and cuprate-based high temperature superconductors has been actively investigated [1–5]. Many reports have pointed out that pyridyl nitrogens strongly adsorb on Au(111) surfaces or Pt(111) surfaces, much in the same way as thiol sulfurs do [5]. Recently, nanostructural materials, especially gold nanoparticles, have attracted con-

siderable attention because of their potential application as the promising optical devices and nanoelectronic devices due to their high surface-to-volume ratios and small size effect [6–19]. These nanocomposites own special nonlinear optical behaviors that are absent in individual atoms as well as bulk materials. It has been demonstrated that silver can be encapsulated inside poly dendrimers. This nanocomposite displays a drastic optical extinction by a factor of 115, which arises from nonlinear scattering [19]. However, few investigations have been carried out for optical nonlinearities in these nanostructured materials, especially for the nanocomposites with zerovalent metal nanoparticles [17,18,20]. In the present Letter two novel [60]fullerene derivatives containing the oligopyridyl group have been synthesized and self-assembled on

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Scheme 1.

the surface of gold nanoparticles to investigate the nonlinear optical responses. The synthetic routes leading to the two [60]fullerene derivatives are presented in Scheme 1. For convenience, the gold nanoparticles stabilized by the C60BPY and C60TPY are denoted as the C60BPY-Au and C60TPY-Au, respectively. Both the C60BPY-Au and C60TPY-Au can be dissolved in chloroform. The C60TPY-Au in chloroform displays stronger optical limiting performances than C₆₀ in toluene and C60BPY-Au, which indicates that the optical limiting properties are sufficiently enhanced.

2. Experimental section

2.1. General

For transmission electron microscopy (TEM), a drop of the colloidal gold solution was placed on a carbon-coated Cu grid, and the chloroform allowed evaporating. Specimens were examined in a Hitachi 800 transmission electron microscope.

The nonlinear responses of the two kinds of nanoparticles in chloroform were measured with Nd:YAG laser, which produces 8 ns (FWHM) laser pulses at 532 nm with a repetition rate of 1 Hz. The spatial profile of the pulses is nearly Gaussian. Z-scan technology is a convenient and

easy way to determine nonlinear refraction and nonlinear absorption using single beam laser. Z-scan experiments along the focus axis were performed similar to the literature with exceptions that the probe (without an aperture before it) was placed after the sample [21]. Thus the influence of the instability of the laser pulse energies on measured results can be ruled out. In the experiment the pulse energy of 150 μJ is used. The linear transmission of the sample solution placed in the quartz cell of a thickness of 1 mm is 87%.

Optical limiting measurements were performed. The sample placed in a quartz cell of thickness 2 mm located at the focus of a lens with a focal length of 30 cm. Both the incident and transmitted laser pulse energies were monitored simultaneously by using two energy detectors (Rjp-735 energy probes, Laser Precision), respectively.

2.2. Materials

4-(Bromomethyl)-4'-methyl-2,2'-bipyridine (**2**), 4'-*p*-tolyl-2,2':6',2''-terpyridine and 4'-(*p*-bromomethylphenyl)-2,2':6',2''-terpyridine (**4**) were prepared according to literature procedures, respectively [22–24]. The azides **3** and **5** were obtained following methods similar to those previously described [24] and then used directly to react with C₆₀. C60BPY was obtained as described [25].

2.3. Synthesis of C60TPY

The synthetic method of C60TPY was similar to that of C60BPY [25]. To a solution of C₆₀ (36 mg, 0.05 mmol) in chlorobenzene (30 ml), compound **5** (19 mg, 0.05 mmol) was added. The mixture was stirred and heated to reflux under nitrogen for 24 h. The brown solution was concentrated and the crude solid product was washed with acetone (3 × 20 ml). The resultant solid was then purified by chromatography on silica-gel using chloroform–acetone (30:1, v/v) as eluent to give C60TPY in a yield of 23% (based on converted C₆₀). The FT-IR spectrum (KBr pellet) indicated a band of C₆₀ moiety at 526 cm⁻¹. MS (MALDI-TOF): *m/z* 720 [C₆₀], 1057 [M⁺ + H], 1079 [M⁺ + Na]; ¹H NMR (300 MHz, CD₂Cl₂): δ 4.98 (s, 2H), 7.10–7.35 (m, 4H), 7.99–7.83 (m, 4H), 8.61–8.64 (d, 2H), 8.67–8.73 (m, 4H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 54.08, 99.00, 104.55, 119.27, 123.85, 124.87, 127.35, 127.41, 127.46, 127.65, 127.77, 128.60, 128.82, 128.89, 129.11, 133.27, 135.46, 136.49, 136.90, 137.72, 138.21, 140.48, 141.74, 142.06, 142.30, 142.33, 142.43, 142.55, 142.81, 143.07, 143.84, 144.14, 144.25, 144.44, 144.56, 144.72, 144.76, 145.17, 145.28, 145.52, 145.60, 145.77, 145.93, 146.25, 146.79, 147.06, 147.96, 149.29.

2.4. Preparation of gold nanoparticles

Gold nanoparticles stabilized by C60TPY or C60BPY were prepared through the reduction of [AuCl₄]⁻ by aqueous sodium borohydride in the presence of C60TPY or C60BPY, which was similar to the literature [8]. HAuCl₄ (0.01 mmol) in deionized H₂O (5 ml) was added to the solution of a phase transfer catalyst *n*-Oct₄ NBr (0.2 mmol) in CHCl₃ (5 ml) and the resulting mixture was stirred vigorously for 10 min. The organic layer was added to the solution of the stabilizer (C60TPY or C60BPY, 0.05 mmol) in CHCl₃ (5 ml). Then the reducing agent (NaBH₄, 0.1 mmol) in H₂O (2 ml) was dropped to the above solution in 10 min. The resulting mixture was stirred overnight at room temperature, filtered, and washed with H₂O (3 × 20 ml). The organic layer was separated and evaporated to about 4 ml and EtOH (20 ml) was added to

precipitate the gold nanoparticles. The crude gold nanoparticles obtained by centrifugation were re-dissolved in CHCl₃ (5 ml) and re-precipitated by addition of EtOH (20 ml). The gold nanoparticles were obtained by centrifugation.

3. Results and discussion

The optical properties of nanoscale metal domains are strongly influenced by the surface plasmon resonance [26]. The absorption spectra of gold nanoparticles in CHCl₃ are shown in Fig. 1. The solution of the gold nanoparticles displays the specific surface plasmon band of gold clusters with a maximum around 560 nm, which is ascribed to a collective oscillation of conduction electrons in response to optical excitation [18,26]. In accordance with the UV–Vis spectrum, the TEM images in Fig. 2 show the actual presence of nanoagglomerated spherical particles with an average radius of 10 nm. These results indicate that gold nanoparticles can be prepared using the C60TPY or C60BPY as stabilizer. It is assumed that there is strong interaction between nitrogen atoms in pyridyl groups and Au surface. Because of the strong interaction between nitrogen atoms and Au surface, the C60TPY or C60BPY containing pyridyl groups could function as the stabilizer of gold nanoparticles similar to thiol derivatives [27].

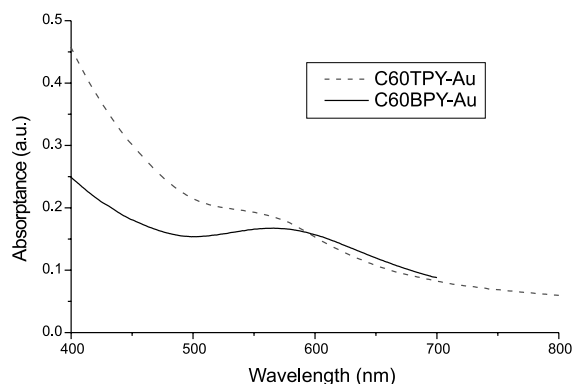


Fig. 1. The absorption spectra of gold nanoparticles in chloroform at room temperature. The C60TPY-Au (dash line) and C60BPY-Au (solid line).

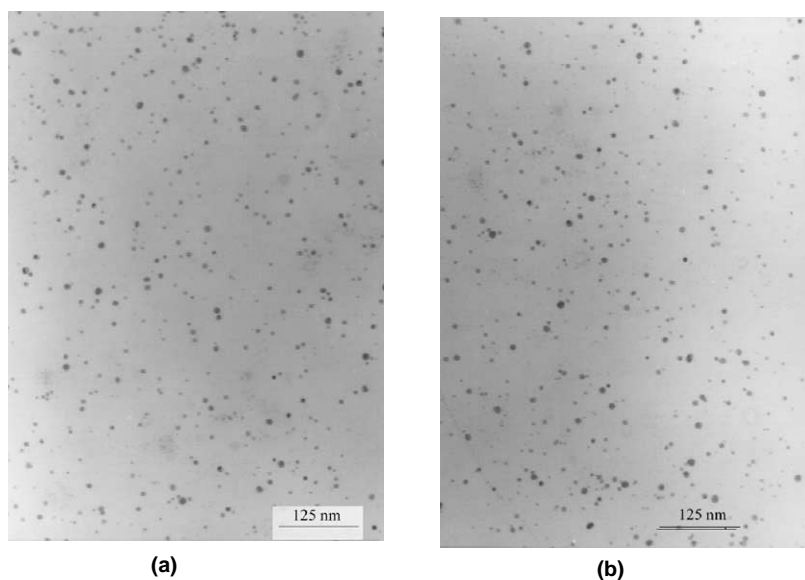


Fig. 2. The TEM images of gold nanoparticles protected by C60TPY (a) and C60BPY (b).

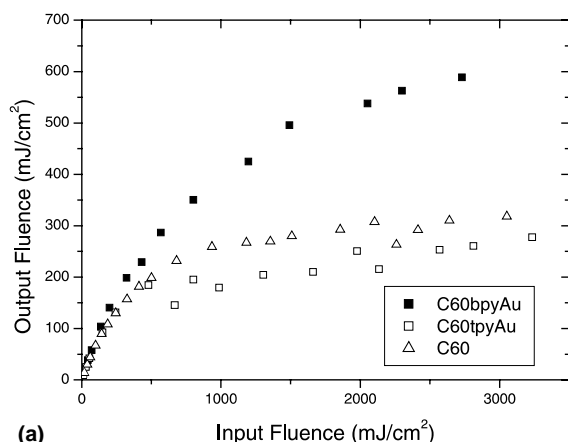
The optical limiting properties of the two kinds of nanoparticles are determined for nanosecond and picosecond pulses, respectively. Fig. 3a gives the experimental results of the two measurements using nanosecond pulses. The absorptive optical limiting of C_{60} in toluene is also measured under the same experimental conditions for comparison. As it is shown, distinct differences between the optical limiting properties of C60TPY-Au and C60BPY-Au can be observed. C60TPY-Au in chloroform displays stronger optical limiting performances than C_{60} in toluene and C60BPY-Au in chloroform, which indicates that the optical limiting properties are sufficiently enhanced.

Similar distinct differences in the picosecond optical limiting properties between the C60TPY-Au and C60BPY-Au can also be observed (Fig. 3b). The optical limiting properties of C60TPY-Au and C60BPY-Au were measured using 40 ps laser pulses with the linear transmission of 75%. Large optical limiting responses of both C60TPY-Au and C60BPY-Au nanoparticles in solution were observed. The picosecond optical limiting of C60TPY-Au was superior to that of C60BPY-Au. As shown in Fig. 3b, the nonlinear transmission of C60TPY-Au solution was decreased to 80 mJ/cm²

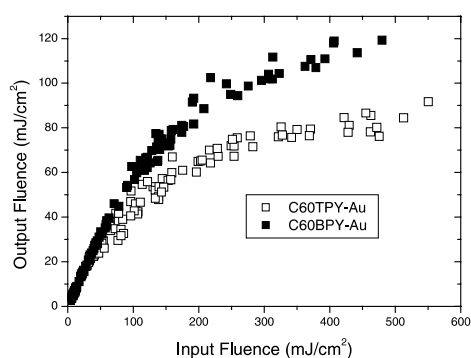
at an input fluence of 600 mJ/cm², while it was decreased to 120 mJ/cm² at an input fluence of 500 mJ/cm² for C60BPY-Au solution.

Although the difference between the optical limiting properties of C60TPY-Au and C60BPY-Au was distinct, the difference between the optical limiting properties of C60TPY and C60BPY was weak (Fig. 4). Meanwhile, the optical properties of the C60TPY-Au at both picosecond and nanosecond scales were better than that of the C60BPY-Au with almost the same size. These differences resulted from different interaction of the gold nanoparticles with C60TPY and C60BPY. It was attested by the Z-scan results.

The nonlinear absorption was measured from the normalized energy transmission using Z-scan technique without an aperture. The experimental results indicate that both C60TPY-Au and C60BPY-Au nanoparticles in chloroform show strong nonlinear absorption (Fig. 5). And differences between the nonlinear absorption and refraction of C60TPY-Au and C60BPY-Au were observed. The lower valley of the normalized transmissions of 0.28 for the C60TPY-Au chloroform solution, as compared to that of 0.38 for the C60BPY-Au chloroform solution, indicates that



(a)



(b)

Fig. 3. (a) The nanosecond optical limiting results of the C60TPY-Au in chloroform, C60BPY-Au in chloroform, and C₆₀ in toluene with the identical linear transmission of 81%. (b) The picosecond optical limiting results of the C60TPY-Au in chloroform and C60BPY-Au in chloroform with the identical linear transmission of 75%.

the nonlinear absorption of the former is stronger than the latter. So the distinct difference in Z-scan experimental results without an aperture between the two kinds of nanoparticles mainly arises from the stronger interaction of the C60TPY with the gold surface than that of the C60BPY.

Fig. 5 shows the results of Z-scan data with an aperture (linear transmission $S = 0.1$) divided by those without an aperture. It has been reported that fullerenes and fullerene derivatives possess only relatively weak excited-state refraction (generally weak self-defocusing effects), although they display the strong excited-state absorption in visible and near infrared range [28–30]. The [60]fullerene derivatives of C60BPY and C60TPY

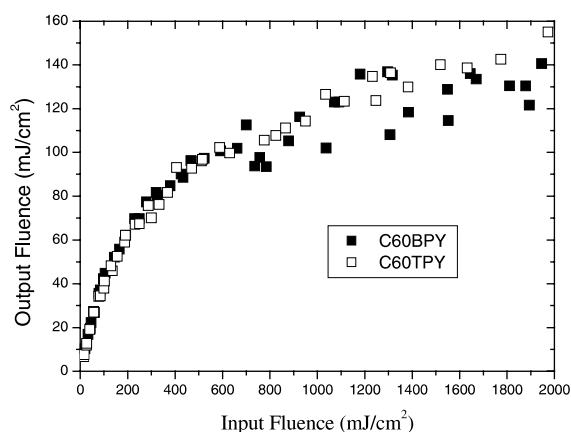


Fig. 4. The nanosecond optical limiting results of the C60TPY in chloroform, C60BPY in chloroform, and C₆₀ in toluene with the identical linear transmission of 51%.

in the two kinds of nanoparticles are similar to C₆₀ and it can be assumed that they could possess only weak self-defocusing behaviors. But as it can be seen in Fig. 5, both chloroform solutions of C60TPY-Au and C60BPY-Au display strong nonlinear refractions (self-focusing effects in this case). We suppose that it results from the surface plasmon resonance of the gold nanoparticles caused by light excitation. The results may show that the nonlinear refractions of these nanoparticles result from the interband transition, to the large extent, due to the surface plasmon resonance. Meanwhile the latter possesses much stronger nonlinear refraction owing to its larger peak-valley difference of 0.55 under the normalized transmissions condition, as compared to that of 0.34 for the former. The difference of nonlinear refractions in these nanoparticles results from the different interactions between the gold surface and the stabilizer C60BPY and C60TPY.

It should be noted that the peak-valley positions of the normalized transmissions in Fig. 5c are not symmetrical with respect to the focus ($Z = 0$) and the peak value is much low. We suppose that it is induced by nonlinear scattering resulting from the formation of scattering centers [19]. On the other hand, as compared to the depressed valley of the normalized transmissions of Z-scan without an aperture shown in Fig. 5a, the valley observed in Fig. 5c is pronounced. This could be contributed

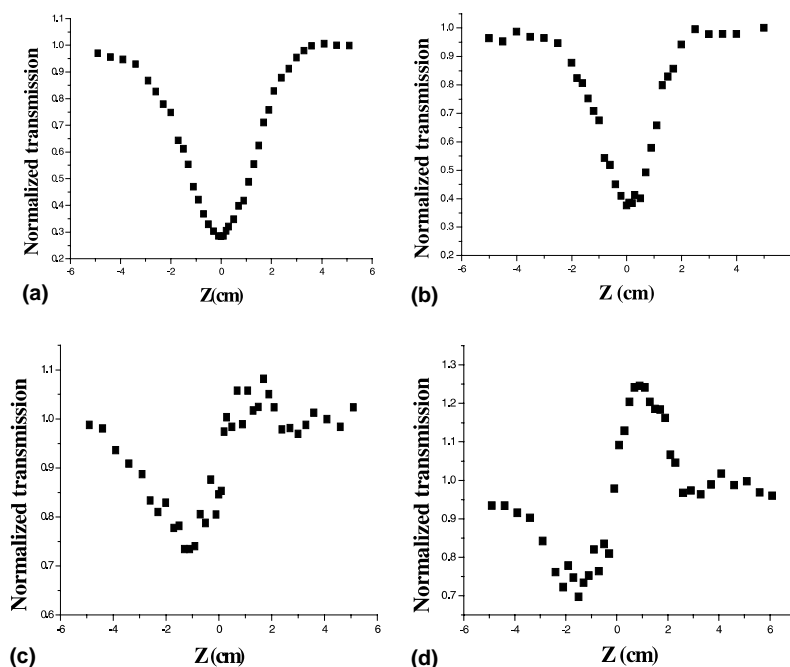


Fig. 5. The normalized transmission data of Z-scan without an aperture for C60TPY-Au in chloroform (a) and C60BPY-Au in chloroform (b) with the identical linear transmission of 87% and the normalized transmission results of Z-scan data with an aperture (the linear transmission of $S = 0.1$) divided by those without an aperture for (c) C60TPY-Au in chloroform and (d) C60BPY-Au in chloroform with the identical linear transmission of 87%.

to not only the nonlinear absorption including the excited-state and the surface plasmon absorptions, but also the nonlinear scattering of the C60TPY-Au solution in chloroform. To our surprise, the nonlinear scattering can hardly be found in the C60BPY-Au chloroform solution, as confirmed by the symmetrical peak-valley as shown in Fig. 5d. It is considered that the nonlinear absorption in the C60BPY-Au chloroform solution is not strong enough to result in distinct nonlinear scattering.

4. Conclusion

The nonlinear optical responses of the gold nanoparticles stabilized by the two novel [60]fullerene derivatives have been performed with nanosecond laser pulses. The results indicate that their nonlinear absorptions and the nonlinear refractions are dependent on the interaction between the gold surface and the stabilizer [60]fullerene derivatives C60BPY and C60TPY.

Acknowledgements

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