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ARTICLE TYPE

Tuning aggregation mode induced different chirality in organogels of mono- and bis-triterpenoid derivatives and preparation of gold nanoparticles as a template

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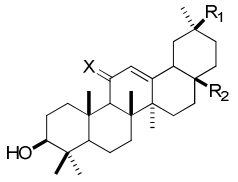
The new gelators based on chiral triterpenoids linked with aromatic rings and amide structures were designed and synthesized. Different chiral properties of assembly in the organogels were observed expressed by different close degree of molecular packing, which was attributed to the formation of H-type aggregates in the monotriterpenoid and J-type aggregates in the bis-triterpenoid derivatives. The nanofibers of the organogel in DMSO were used to engineer gold nanoparticles and generate gel-nanoparticle hybrid materials.

Introduction

Nanoscale materials from small molecules which could spontaneously and controllably self-assemble into three-dimensional networks with solvent molecules entrapped in cavities were supramolecular gels.[1] Generally, weak non-covalent interactions such as van der Waals interactions, hydrogen bonding, π-π stacking, electrostatic interactions, coordination interactions, and host-guest interactions[2] promoted these small molecules called low-molecular-weight gelators (LMWGs)[3] to aggregate. This functional material has attracted much attention because of a wide range of applications, such as drug delivery,[4] tissue engineering,[5] light-harvesting systems,[6] catalysis of organic reactions,[7] and optoelectronics.[8] The fibrillar network structures of gel matrix could provide porous pockets filled with solvents and they can accommodate nanomaterial hosts such as nanoparticles and nanotubes to construct nanohybrid material.[9] This hybrid gel exhibit interesting and different physicochemical properties compared with the native gel. [10] Rao *et al*. incorporated single-walled CNTs (SWCNTs) into organogel from L-alanine gelators to obtain gel–CNT composites.[11a] Banerjee and co-workers made pyrene-conjugated peptide-based fluorescent organogel to act as excellent host for the incorporation of graphene, which lead to more rigid hybrid gel.[11b]

Chiral information of molecular scale can be translated into nanoscale assemblies as a consequence of spatial arrangements controlled by non-covalent interactions, [12] which means supramolecular chirality. Therefore, gelation which resulted from gelators aggregation could deliver the molecular packing information into suparmolecular gels and induced supramolecular chirality consequently if the gelators are chiral molecules. [13]

Because of readily modification and ability for bottom-up aggregation, natural products, such as amino acids, carbohydrates, fatty acids, steroids, and porphyrins, are attractive building blocks to design low molecular weight gelators.[14] Among them, pentacyclic triterpenoids such as glycyrrhetinic acid (GA) and oleanolic acid (OA) (Fig. 1) have been well known for their biological activities such as anti-inflammatory, antitumour, anti-virus and anti-fungal.[15] Due to special characteristics such as chiral rigid skeletons, relative low toxicity and biocompatibility, previously this kind of natural product have been used to construct supramolecular gels.[16] For example, Bag and co-workers[17] reported that betulinic acid, glycyrrhetinic acid and oleanolic acid without any chemical modifications can gelate different organic solvents, which suggest the aggregation trend of this skeleton in suitable solvents. As we know, cholesterol-based compound of $A(LS)_2$ type, where A stands for aromatic component, S steroid moiety and L a linker connecting the two units, was a typical kind of LMWG.[18] However, there have not been reports on self-assembly of triterpenoids derivatives like this type. As our continuous work [19]and in order to develop new gelators based on triterpenoids, here we study the gelation properties of mono- and bis-triterpenoid derivatives (**GA-1**/**2** and **OA-1**/**2**) containing aromatic rings and amide structures (Scheme 1) and the different packing arrangement of the gelators, which resulted in different chiral properties of the assembly. In addition, the nanostructures present in the organogel of DMSO were exploited as templates to synthesize gold nanoparticles (AuNPs).

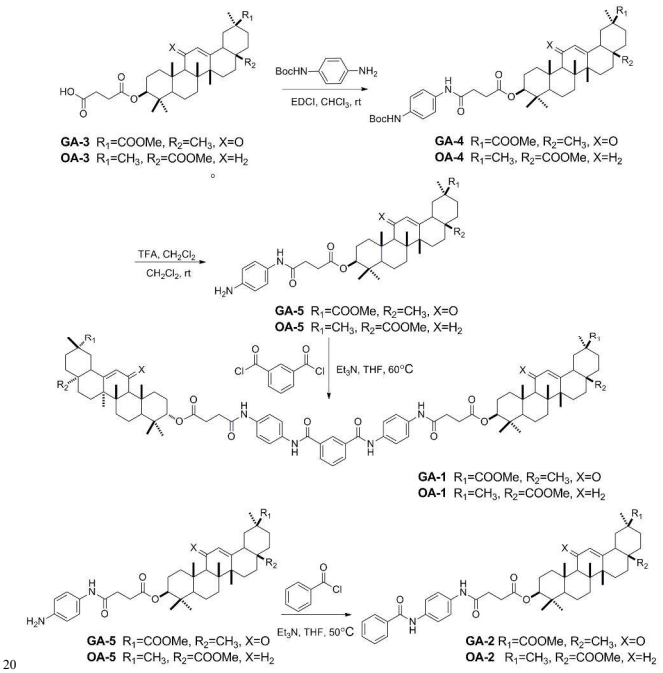


GA R_1=COOH, R_2=CH_3, X=O
OA R_1=CH_3, R_2=COOH, X=H_2

Fig. 1 Structure of Glycyrrhetinic acid (GA) and Oleanlic acid (OA)

Results and discussion

The gelling behaviors of the four compounds in various solvents were studied using the "stable to the inversion of a test tube" method. [20] The solid gelator and solvent were put into a sealed bottle and heated until the solid dissolved. Then, the solution was treated with ultrasound and then cooled to room temperature. The bottle was subsequently inverted to determine the gel formation. Both the mono- and the bis-triterpenoid derivatives were observed to form stable gels in some organic solvents. Their gelation abilities were summarized in Table 1. Due to the different solubility in the solvents, there are some different gelation abilities between derivatives based on **GA** and **OA**.[19d, 21] Dimer of **GA** (**GA-1**) could only form stable gel in DMSO, however dimer of **OA** (**OA-1**) could form gels in some aromatic solvents (Figure S1). As for the monotriterpenoid derivatives, both **GA-2** and **OA-2** could gel aromatic solvents strongly (Fig. 2). The four compounds, were freely soluble in solvents such as chloroform, DMF and THF.



Scheme 1 Synthesis of the gelators.

Table1. Gelation properties of gelators **GA-1**, **OA-1**, **GA-2** and **OA-2** in different solvents

Solvent	GA-1	OA-1	GA-2	OA-2
toluene	I	I	G(1.50)	G(0.77)
benzene	I	I	G(1.20)	G(1.10)
o-xylene	I	I	G(0.40)	G(0.57)
m-xylene	I	I	G(0.35)	G(0.62)
p-xylene	I	I	G(0.60)	G(0.70)
mesitylene	I	I	G(1.10)	G(0.96)
chlorobenzene	I	G(1.90)	G(1.00)	G(0.88)
dichlorobenzene	I	G(2.00)	G(0.80)	G(1.00)
bromobenzene	I	G(1.60)	S	G(1.10)
chloroform	P	P	S	S
THF	S	S	S	S
DMSO	G(1.00)	S	S	S
methanol	P	P	I	I
DMF	S	S	S	S
n-hexane	P	P	P	P

G=gel, P=precipitate, S= solution, I=insoluble. The number in parentheses is the MGC (minimum gelator concentration) of the system (g/100 cm^3)

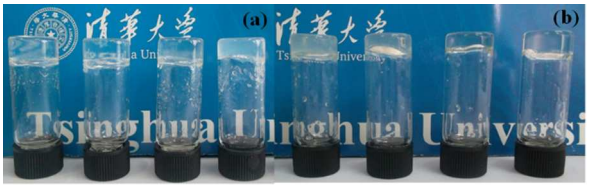


Fig. 2 Gels containing (a) **GA-2** in chlorobenzene, o-xylene, dichlorobenzene, mesitylene (b) **OA-2** in p-xylene, chlorobenzene, dichlorobenzene, o-xylene (from left to right)

In order to obtain good insight into the molecular aggregation within the gels, the morphology of the xerogels was investigated by scanning electron microscopy (SEM) and transmission electron microscope (TEM). As shown in Figure 3, the xerogel of **GA-1** in DMSO showed typical self-assembled fibrillar networks commonly observed in gels with regular diameters of about 200 nm. The gelator **OA-1** facilitated the formation of super bundles with micrometer range diameters and entangled rope-like structures (See Figure S2). The morphology of the xerogel prepared from monotriterpenoid showed a network structure composed of nanoscale fibrous aggregates with the diameters in the range of 20-100 nm. They were formed by hierarchical self-organization of gelators and then further entangled together to fibres and finally interconnected to network (Fig. 4a, 4b, 4c). TEM studies offered a closer look at the self-assembled structures of fibre network (Fig. 4d).

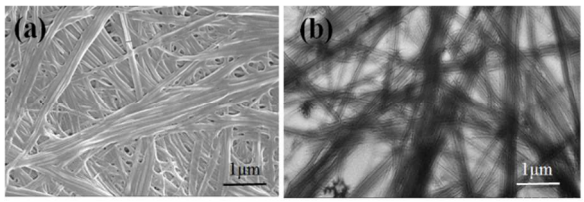


Fig. 3 (a) Scanning electron micrographs and (b) transmission electron micrographs of gels from **GA-1** in DMSO.

^{1}H NMR spectroscopy technique was used to study the driving forces for the formation of organogels. As a typical example, the ^{1}H NMR spectra of **GA-1** in DMSO-d_6 at 25-100 ºC was shown in Figure 5. Due to the immobilization of the organic molecules in the gel phase at room temperature, the gel sample displayed broad and less resolved signals. At 90 ºC, as the gel sample converted into solution, the signals became well-resolved and the chemical shift of amide protons notably upfield shifted 0.28 and 0.32 ppm respectively. This upfield shift implied that hydrogen-bond interactions became weaker at elevated temperature and such interactions probably played an important role in mediating the assembly of gelators. Thus, the temperature-dependent ^{1}H NMR study was also performed using the organogel of **OA-2** in C_6D_6 (Figure S3). When recorded at room temperature, the gel sample displayed poor resolved signals, so we chose the spectra from the temperature 40 ºC at which the gel gradually showed fluidity. As temperature increased from 40 ºC to 65 ºC, the amide protons notably upfield shifted and aromatic protons upfield shifted which implied π-π interaction between aromatic groups played a synergic role with hydrogen bonding for gel formation.

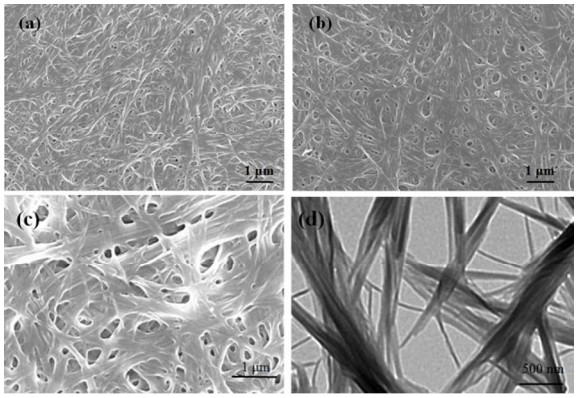


Fig. 4 (a) Scanning electron micrographs of gels from **OA-2** in chlorobenzene (b) **OA-2** in dichlorobenzene (c) **GA-2** in dichlorobenzene (d) transmission electron micrographs of gels from **GA-2** in o-xylene.

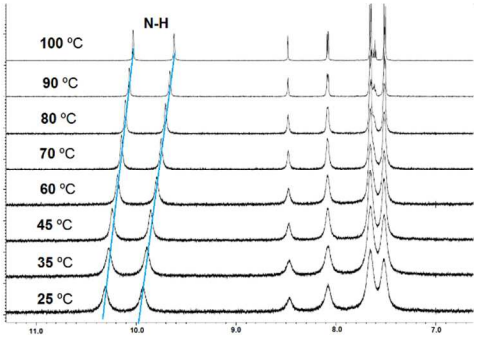


Fig. 5 Variable temperature ^{1}H NMR (600 MHz) of gel **GA-1** from DMSO-d_6

Generally, molecular scale chiral information can translate into nanoscale architectures through self-assembly processes and then into the macroscopic behaviour of the gels. However, the chiral morphologies present in a gel can be highly dependent on the methods for gel formation, for example rate of cooling and sonication etc.[22] In some cases, the chirality of the nanoscale objects can be clearly visualised using SEM or TEM, but these microscopies more usually detect the presence visualise fibres, consisting of bundles of molecular-scale fibrils.[12b] So Circular dichroism (CD) spectroscopy is one of the best methods for investigating nanoscale chiral organisation. Here, to obtain more information about the nature of the self-assembled structures, the CD spectra of organogels were examined. As shown in Figure 6, organogels of **GA-1** and **GA-2** were both observed CD signal around 319 nm and 306 nm respectively contrasted with the CD silence at the solution state. It indicated that chiral information of treterpenoid skeleton translated into aggregates as a consequence of spatial arrangements and the gels were chiral aggregates.

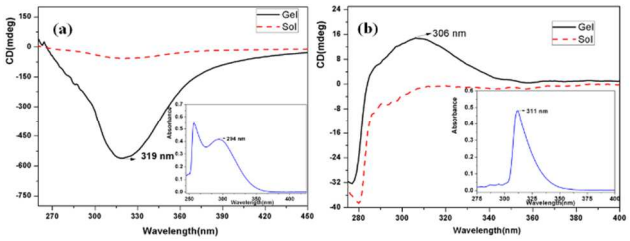
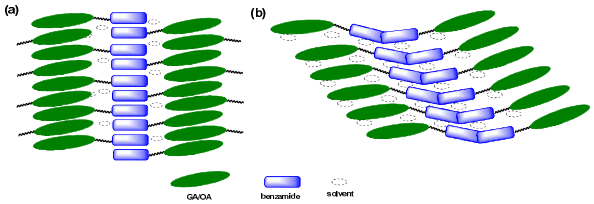


Fig. 6 CD spectrum of gel and solution of (a) **GA-1** (b) **GA-2** (Insert were UV-vis of dilute solution)

Notably, for the monotriterpenoid derivative **GA-2**, the CD signal of the organogel was less intense at the nearly same concentration with the bis-triterpenoid, which demonstrated that different types of molecules exhibit different ability to express chiral properties. It could be related to the close degree of gelators arrangement and the different packing mode.[23] In addition, it was noted that the UV-vis maximum absorption of **GA-1** in dilute solution of DMSO was at 294 nm, so a bathochromic shift was observed in CD spectrum of organogel (Fig. 6a). In contrast to **GA-1**, the absorption band for **GA-2** in dilute solution of O-xylene was at 311 nm and a blue shift was observed in CD spectrum of organogel (Fig. 6b). The bathochromic shift in the absorption band of **GA-1** with the formation of organogel indicate that the aromatic groups of **GA-1** packed with slipped stack or a head-to-tail fashion (J aggregates), however the aromatic groups of **GA-2** aggregates in organogels adopted cofacial arrangements (H aggregates).[24] As for bis-triterpenoid derivative, two triterpenoids blocked the aromatic core to pack in a face-to-face fashion (H aggregates). The change in the nature of the aggregate from the H type in the monotriterpenoid derivative to the J type in the bis-triterpenoid derivative should be related to the different molecular structure.[25] In the bis-triterpenoid derivatives, J type arrangement of the linker core by π-stacking and hydrogen-bond interactions induced the loose aggregate of triterpenoids, which made the chirality easy to express into advanced level. In contrast, H type arrangement of the linker core in monotriterpenoid derivative lead to the close arrangement of triterpenoids, which resulted the less chiral property compared with the bis-triterpenoid derivatives. On the basis of the above discussions, representation of the self-

assembly was shown below (Scheme 2).



Scheme 2 Probable mode of self-assembly of gelators (a) monotriterpenoid (b) bis-triterpenoid derivatives

Hybrid materials such as gold nanoparticles (AuNPs)-gel hybrid nanomaterial attracted considerable attention because of easy synthesis of nanoparticles and potential application in catalysis, optics, and SERS.[26] Generally, the gel fibers could sustain metal nanostructures and provide a framework to stabilize the NPs.[27] Herein, we used the nanostructures present in the organogel of **GA-1** in DMSO as a template to situ synthesize gold nanoparticles (AuNPs).[28] Firstly, the **GA-1** organogel in DMSO containing a gold precursor ($HAuCl_4 \cdot 3H_2O$) was prepared (Fig. 7a). Then a reducing agent such as tetrabutylammonium borohydride was added on the top of the gel layer to reduce Au(III) to Au(I) and a purple-black gel-AuNPs hybrid material was obtained (Fig. 7b). SEM (Fig. 7c) and TEM (Fig. 8a) indeed showed the presence of gold nanocrystals with diameter 5-30 nm embedded on the fibers of the organogel. The ellipsoidal and spherical shapes of the nanocrystals structures of AuNPs were observed. Surface plasmon resonance (SPR) band was at 538 nm, indicating the presence of large and different shapes of gold nanocrystals in the hybrid material (Fig. 8b).

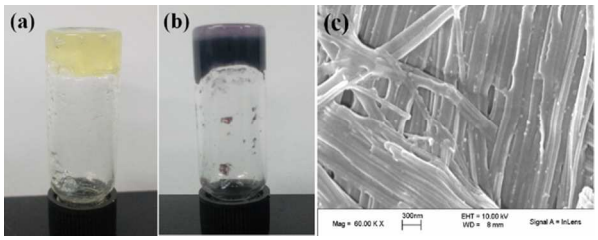


Fig 7. (a) (b) Preparation of AuNPs with **GA-1**/DMSO organogel. (c) The fibrillar network of the AuNPs/organogel hybrid material.

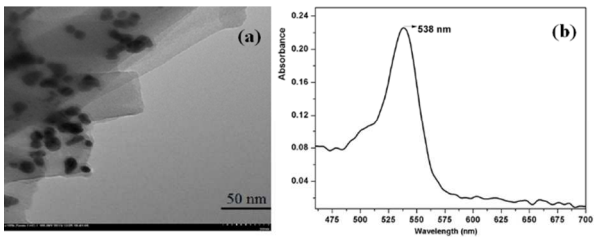


Fig 8. (a) TEM images of gold nanocrystals of different shapes on the surface of the gel fibers (b) SPR band of the AuNPs in the hybrid gel

Conclusions

The new mono- and bis-triterpenoid derivatives were shown to possess the organogelation property. Different chiral properties of the aggregates in the organogel were attributed to the molecular aggregates formed H-type aggregates in the monotriterpenoid derivative and J-type aggregates in the bis-triterpenoid derivative. The J-type aggregates could lead to the loose packing and eventually made it easy to express molecular chirality into assemble level. The organogel based on biocompatible natural facile triterpenoid was used to synthesize gold nanoparticles (AuNPs) as a template and could sustain and stabilize metal nanostructures. Advanced applications of this hybrid material will be further explored in our lab.

Experimental

Materials and methods

Isophthaloyl dichloride, TFA and EDCI were obtained from Alfa Aesar. Other reagents and solvents were purchased from Beijing Chemical Company and used without further purification unless otherwise stated. **GA-3** and **OA-3** were prepared and characterized according to previously published procedures.[19d] NMR spectra were recorded on a JOEL JNM-ECA 300 and 400 spectrometer; Electrospray ionization mass spectrometry (ESI-MS) was measured by Bruker ESQUIRE-LC spectrometer; Scanning electron microscopy (SEM) was performed on LEO-1530, operating at accelerating voltages of 10 kV and samples were placed on the glass and coated with gold; Transmission Electron Microscope (TEM) was acquired on Hitachi H-7650B instrument; UV-Vis spectra was measured with TU-1901; Circular dichroism (CD) spectra were carried on a Pistar π-180 instrument (Applied Photophysics Ltd) with a 150 w xenon lamp as the light source.

Synthesis of compound GA-4 and OA-4

GA-4: To the solution of 500 mg (0.86 mmol) of **GA-3** in 5 ml of dry $CHCl_3$, 198 mg (1.03 mmol) of EDCI and Boc protected p-Phenylenediamine were added. The reaction mixture was stirred at room temperature for 48 h. The mixture was then washed with water (30 ml) and brine (30 ml), dried by $MgSO_4$ and evaporated. The solid was purified by silica gel column chromatography (PE: $CH_3CO_2C_2H_5$ = 4:1) afforded **GA-4** as a yellow solid (363 mg, 56%). ESI-MS m/z: 797.8 $[M+Na]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.54 (s, 1H, -NH), 7.30 (d, 2H, J=8.6 Hz), 7.20(d, 2H, J=7.9 Hz), 5.56 (s, 1H, 12-H), 4.44 (m, 1H, 3-H), 3.60 (s, 3H,30-$COOCH_3$), 1.46 (s, -$(CH_3)_3$, 9H), 0.70, 0.77, 0.79, 1.03, 1.06, 1.08, 1.36 (7×s, 7×3H, 23, 24, 25, 26, 27, 28, 29-CH3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 200.19 (11-C), 176.94 (30-C), 172.65 (3-OCO-), 169.95 (-NH-COCH2-), 169.75 (13-C), 153.21 (-NH-COO-), 134.69 (benzene-C), 133.43 (benzene-C), 120.73 (12-C), 120.73 (benzene-C), 119.28 (benzene-C), 80.94 (3-C), 77.84(O-$C(CH_3)_3$), 61.63, 60.40, 54.92, 53.61, 51.77, 48.35, 45.38, 43.98, 43.17, 41.00, 38.69, 32.58, 31.77, 31.06, 29.85, 28.50, 28.38, 28.26, 28.00, 26.38, 23.51, 23.31, 21.02, 18.61, 17.30, 16.71, 16.38, 14.18.

OA-4: The compound **OA-4** was synthesized using the same procedure as that described for **GA-4**. ESI-MS *m/z*: 762.0 $[M+H]^+$, 783.8 $[M+Na]^+$, 799.6 $[M+k]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.98 (s, 1H, -NH), 6.68 (s, 1H, -NH), 7.23 (d, 2H, J=8.94 Hz), 7.35(d, 2H, J=8.94 Hz), 5.24 (s, 1H, 12-H), 4.50 (m, 1H, 3-H), 3.60 (s, 3H, 28-$COOCH_3$), 1.48 (s, -$(CH_3)_3$, 9H), 1.21, 0.90, 0.88, 0.87, 0.82, 0.82, 0.70 (7×s，7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 178.43(28-C), 173.97(3-OCO-), 169.84(-$NHCOCH_2$), 153.03 (-NHCO-), 143.83 (13-C), 134.41 (benzene-C), 133.41(benzene-C), 122.35 (12-C), 120.77 (benzene-C), 119.36 (benzene-C), 81.65 (3-C), 81.20(O-

$C(CH_3)_3$), 60.49, 55.38, 51.62, 47.60, 46.79, 45.91, 41.69, 41.35, 39.35, 38.14, 37.83, 36.98, 33.92, 33.18, 32.63, 32.46, 32.11, 30.75, 30.00, 28.45, 28.14, 27.75, 25.98, 23.71, 23.59, 23.46, 23.12, 22.75, 18.26, 16.89, 16.79, 15.41, 14.27.

Synthesis of compounds GA-5 and OA-5

GA-5: To the solution of 300 mg (0.86 mmol) of **GA-4** in 7 ml of CH_2Cl_2, 1.4 mL TFA was added at 0 ºC. The reaction mixture was stirred at room temperature for 10 h. The mixture was then washed with saturated $NaHCO_3$ solution, water (30 ml) and brine (30 ml), dried by $MgSO_4$ and evaporated. The solid was purified by silica gel column chromatography (CH_2Cl_2: CH_3OH = 100:1) afforded **GA-5** as a yellow solid (233 mg, 89%). ESI-MS *m/z*: 675.6 $[M+H]^+$, 697.6 $[M+Na]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.69 (s, 1H, -NH), 7.22 (d, 2H, J=8.58 Hz) 6.59(d, 2H, J=8.58Hz), 5.64 (s, 1H, 12-H), 4.52 (m, 1H, 3-H), 3.66 (s, 3H,30-$COOCH_3$), 3.26 (s, -NH_2, 2H) 1.34, 1.13, 1.13, 1.10, 0.85, 0.85, 0.78 (7×s，7×3H, 23, 24, 25, 26, 27, 28, 29-CH_3), ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm) 200.19 (11-C), 177.04 (30-C), 173.01 (3-OCO-), 169.63 (-$NHCOCH_2$-), 169.48 (13-C), 143.26 (benzene-C), 129.45 (benzene-C), 128.52 (benzene-C), 122.03 (12-C), 115.46 (benzene-C), 81.29 (3-C), 61.78, 55.10, 51.86, 48.49, 45.49, 44.12, 43.29, 41.15, 38.84, 38.19, 37.82, 37.00, 32.74, 32.08, 31.91, 31.20, 30.14, 28.60, 28.40, 28.15, 26.54, 23.64, 23.43, 18.74, 17.42, 16.79, 16.48.

OA-5: The compound **OA-5** was synthesized by using the same procedure as that described for **GA-5**. ESI-MS *m/z*: 661.8 $[M+H]^+$, 683.7 $[M+Na]^+$, 699.6 $[M+k]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.87 (s, 1H, -NH), 7.20 (d, 2H, J=8.94 Hz), 6.55(d, 2H, J=8.58 Hz), 4.50 (m, 1H, 3-H), 3.62 (s, 3H, 28-$COOCH_3$), 1.21, 0.88, 0.87, 0.86, 0.83, 0.82, 0.71(7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 177.51(28-C), 173.09(3-OCO-), 169.72(-NHCO-), 143.313 (13-C), 138.22 (benzene-C), 129.46(benzene-C), 127.95(benzene-C), 122.07 (12-C), 115.38 (benzene-C), 81.56 (3-C), 55.49, 51.65, 48.58, 44.40, 41.46, 41.24, 38.57, 37.89, 37.29, 36.96, 35.79, 34.93, 33.19, 32.71, 32.20, 31.96, 28.15, 27.14, 25.22, 24.22, 23.72, 22.76, 24.72, 21.13, 18.27, 17.42, 16.75, 16.49

Synthesis of compound GA-1 and OA-1

GA-1: 430 mg (0.63 mmol) **GA-5** and Et_3N (100 µL) were dissolved in 15 ml dry THF and cooled in ice bath. 69 mg (0.32 mmol) isophthaloyl dichloride was added to the reaction mixture. The reaction mixture was stirred at 60 ºC for 5 h. The reaction mixture was filtered and evaporated in vacuum to solid. Purification was done by silica gel column (100-200 mesh) using CH_2Cl_2: CH_3OH =30:1 as eluent to give **GA-1** as a white solid (450 mg，48%). ESI-MS *m/z*: 1516.4 $[M+Cl]^-$, ^1H NMR ($CDCl_3$: CD_3OD=4:1, 400 MHz, δ ppm): 9.49, 9.08 (2×d, 2H, -NH), 8.27 (s, 1H, benzene), 7.96 (d, 2H, benzene), 7.52~7.40 (m, 9H, benzene), 5.54(s, 1H, 12-H), 4.44~4.41 (m, 2H, 3-H), 3.62 (s, 6H, 30-$COOCH_3$), 1.27, 1.05, 1.04, 1.02, 0.78, 0.78, 0.70 (7×s, 7×3H, 23, 24, 25, 26, 27, 28, 29-CH_3) ^{13}C NMR ($CDCl_3$ and CD_3OD, 100 MHz, δ ppm): 200.81(11-C), 177.39(-$COOCH_3$), 173.21(-COO-), 170.50(13-C) 170.37, 165.96(-CONH-), 135.01, 134.92, 134.11, 130.85, 129.07, 128.18, 125.63, 121.27, 120.45, 81.40, 61.71, 54.97, 53.44, 45.47, 44.09, 43.27, 41.00, 38.69, 38.06, 37.70, 36.91, 32.60, 31.81, 31.48, 31.03, 29.79, 28.46, 28.21, 27.95, 26.40, 26.31, 23.44, 23.27, 18.59, 17.29, 16.59, 16.32.

OA-1: The compound **OA-1** was synthesized by using the same procedure as that described for **GA-1**. ESI-MS *m/z*: 1488.2 $[M+Cl]^-$, ^1H NMR (DMSO-d_6, 400 MHz, δ ppm): 10.34, 9.96 (2×d, 4H, -NH), 8.50 (s, 1H, benzene), 8.12 (d, 2H, benzene), 7.71~7.54 (m, 9H, benzene), 4.45~4.40 (m, 2H, 3-H), 3.57 (s, 6H, 28-$COOCH_3$), 1.13, 0.93, 0.84, 0.83, 0.80, 0.80, 0.71(7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3) ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm):176.67 (30-$COOCH_3$), 172.42 (3-COO-), 170.07 (13-C), 165.25, 162.60 (-CONH-), 138.24, 135.80, 135.72, 134.68, 133.24, 131.01, 130.15, 129.11, 127.86, 127.39, 121.30, 119.67, 80.50, 61.03, 55.17, 52.05, 50.32, 48.42, 44.45, 41.38, 41.27, 37.91, 37.26, 36.96, 35.72, 34.87, 32.83, 32.42, 31.86, 28.23, 27.11, 25.94, 24.36, 23.55, 21.31, 18.28, 17.69, 17.07, 16.64.

Synthesis of compound GA-2 and OA-2

GA-2: 100 mg (0.14 mmol) **GA-5** and Et_3N (25 µL) were dissolved in 10 ml dry THF and cooled in ice bath. 20 µL (0.16 mmol) benzoyl chloride was added to the reaction mixture. The reaction mixture was stirred at 50 ºC for 1.5 h. The reaction mixture was filtered and evaporated in vacuum to solid. Purification was done by silica gel column (100-200 mesh) using CH_2Cl_2: CH_3OH =40:1 as eluent to give **GA-2** as a white solid (110 mg，95%). ESI-MS *m/z*: 802.0$[M+Na]^+$, 817.8 $[M+K]^+$, ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.25, 8.12 (2×s, 2H, -NH), 7.86 (d, 2H, benzene-H), 7.51~7.41 (m, 7H, benzene-H), 5.64(s, 1H, 12-H), 4.57 (dd, J1=4.6 Hz, J2=11.48Hz, 1H, 3-H), 3.67 (s, 3H, 30-$COOCH_3$), 1.34, 1.13, 1.13, 1.10, 0.85, 0.85, 0.79 (7×s, 7×3H,23, 24, 25, 26, 27, 28, 29-CH_3) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.30(11-C), 177.07(-30$COOCH_3$), 173.07(-COO-), 170.05(13-C) 169.63, 166.01(-CONH-), 134.91, 134.11, 131.86, 130.18, 128.77, 128.50, 127.25, 121.42, 120.74, 81.42, 61.78, 55.08, 51.89, 48.48, 45.49, 44.10, 43.29, 41.13, 38.82, 38.20, 37.82, 36.99, 32.73, 31.91, 31.20, 30.00, 28.61, 28.40, 28.16, 26.53, 26.47, 26.53, 26.47, 23.65, 23.44, 18.74, 17.41, 16.80, 16.49.

OA-2: The compound **OA-2** was synthesized by using the same procedure as that described for **GA-2**. ESI-MS *m/z*: 766.1$[M+H]^+$, 788.1 $[M+Na]^+$, 800.4 $[M+Cl]^-$ ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.25, 8.12 (2×s, 2H, -NH), 7.86 (d, 2H, benzene-H), 7.53~7.37 (m, 7H, benzene-H), 5.25(s, 1H, 12-H), 4.51 (m, 1H, 3-H) 3.61(s, 3H, 28-$COOCH_3$), 1.11, 0.91, 0.90, 0.89, 0.83, 0.83, 0.71 (7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 178.45(-28$COOCH_3$), 173.08(-COO-), 170.69(13-C), 168.94, 166.02(-CONH-), 143.86, 134.87, 134.09, 131.86, 128.77, 127.27, 122.33, 121.53, 120.82, 81.72, 55.36, 51.66, 47.60, 46.80, 45.90, 41.70, 41.34, 39.33, 38.13, 37.83, 36.99, 33.93, 33.19, 32.63, 32.25, 30.77, 29.97, 28.17, 27.75, 26.00, 23.72, 23.61, 18.27, 16.90, 16.82, 15.43.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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