# Nesting complexation of $C_{60}$ with large, rigid $D_2$ symmetrical macrocycles†

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A series of four chiral $D_2$ symmetrical macrocycles, in which two 3,3′-disubstituted Binol units are bridged by conjugated organic spacers of differing lengths and/or electronic properties, have been synthesized and characterized. The four different bridges consist of either ether or ester linkages in combination with either short biphenyl spacers or long diethynylphenyl spacers. NMR, CD spectroscopy, and molecular modeling help rationalize the shape of the cyclic scaffolds and even subtle modifications in the bridging units lead to drastic changes in conformation. The three macrocycles with longer bridging units and/or ester linkages form stable 1 : 1 complexes with $C_{60}$ in toluene. The one with a short spacer and ether linkage does not. The binding constants have been determined with a high degree of accuracy *via* equilibrium-restricted factor analysis; with long spacers and ester linkages log $K_a = 4.37(2)$; with short spacers and ester linkages log $K_a = 3.498(4)$; with long spacers and ether linkages log $K_a = 3.509(2)$.

## Introduction

Large macrocyclic structures with shape-persistent characteristics have been the subject of increasing interest for applications in the field of nanoscience.[1] The conformational stability and rigidity of the covalent cyclic structure is traditionally related to the possible enhancement, through a higher degree of preorganization, of the recognition properties towards suitable inclusion guests. Furthermore, flat, conformationally stable, large cyclic organic structures are an essential component in the assembly of organic nanotubes by supramolecular organization in the third dimension.[2] In addition, the expression and amplification of molecular chirality in supramolecularly assembled architectures is a highly valued tool for the design and characterization of oriented nanoscale assemblies.[3] Since enantioselective sensing is essential for the detection and, in suitable contexts, the separation of optically-active molecular species, nanoscale chirality in the production of oriented nanomaterials has potential in a variety of applications.[4] Binol (1,1′-binaphthyl-2,2′-diol) based synthons have been succesfully used as molecular modules for applications in fields spanning from asymmetric catalysis to materials science,[5] because they are robust, and easily functionalized in several positions of the $C_2$ symmetric aromatic skeleton. Macrocycles incorporating two or more Binol units in a rigid sp or sp$^2$ carbon atom covalent framework have been the subject of several elegant studies on molecular recognition.[6] 3,3′-diformyl Binol derivatives have more recently been used, in conjunction with reductive amination protocols using difunctional amines, for the construction of chiral macrocycles to be used as fluorescent enantioselective sensors for the detection of aminoacids.[7] We have recently reported the synthesis of flat, shape-persistent polyester macrocycles containing two or three binaphthyl units and showing recognition properties towards $C_{60}$.[8] In contrast, the introduction of sp$^3$ carbon atoms, possessing a higher flexibility and conformational mobility with respect to sp or sp$^2$ hybridized carbon atoms, has been, in these latter bodies of work,[7,8] minimal. Along with extending the cavity of the macrocycles, we were also eager to explore new reaction methodologies for the production of elongated chiral, rigid macrocycles with potential recognition properties towards fullerene guests. We report here on a series of chiral macrocycles (Fig. 1) in which two Binol units are joined by a pair of matching organic bridges with spacers of varying length and electronic properties of the π-extended structures, and linkages of differing flexibilities (esters *vs.* ethers linking units).

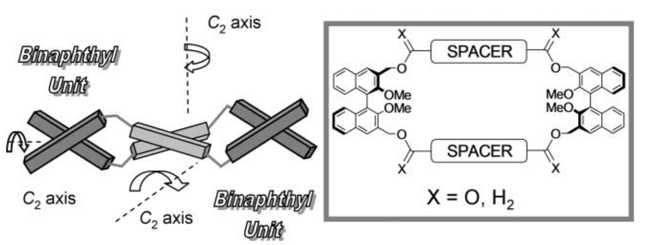


**Fig. 1** Depiction exemplifying the $D_2$ overall symmetry of the macrocycles synthesized and studied (left), and their chemical structures (right).

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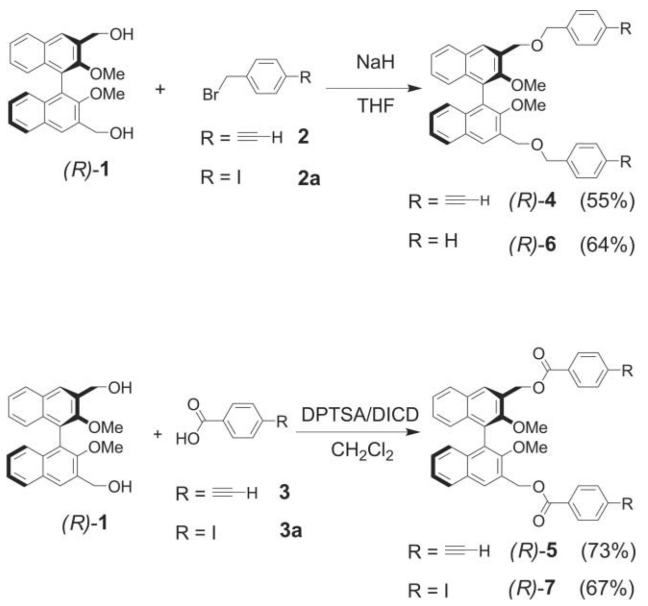
† Electronic supplementary information (ESI) available: Copies of NMR spectra for all compounds, additional NMR and UV/Vis spectroscopic data, and computational details. See DOI: 10.1039/c004379f

## Results and discussion

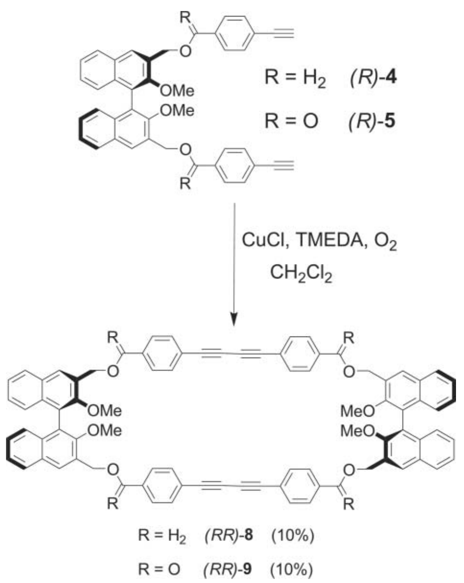
### Synthesis

The synthesis of the molecular modules and of the macrocycles is depicted in Schemes 1 and 2. Elaboration of the known dibenzylic alcohol (*R*)-**1**[9] was carried out by means of the formation of both ether and esters derivatives, in order to introduce elements




**Scheme 1** Synthetic routes to the precursors (DPTSA = 4-dimethylaminopyridinium *p*-toluenesulfonate; DICD = diisopropyl carbodiimide).




**Scheme 2** Synthesis of macrocycles *via* alkyne coupling (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).

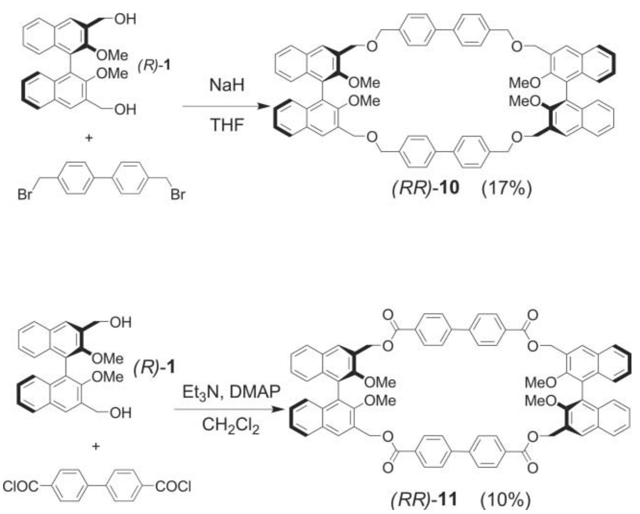
of differing electronic properties and flexibilities, as illustrated in Fig. 1.

Ether precursors (*R*)-**4** and (*R*)-**6** were obtained using standard Williamson ether reaction protocols in good yields (55% and 64%, respectively, after purification by column chromatography), from the known precursor **2**[10] or the commercially-available compound **2a**. Under the strongly basic reaction conditions, however, base-induced iodine exchange occurred so that, in the case of **2a**, iodine-free compound (*R*)-**6** was eventually isolated and characterized as the major product. Ester precursors (*R*)-**5** and (*R*)-**7** were instead obtained using the Moore–Stupp esterification protocol[11] in excellent yields for a direct double coupling (73% and 67%, respectively, after purification by column chromatography) starting from the known precursor **3** or commercially-available **3a**.

When an oxidative alkyne coupling methodology[12] was applied under high dilution conditions to either compounds (*R*)-**4** and (*R*)-**5**, the [2 + 2] macrocycles (*RR*)-**8** and (*RR*)-**9** were obtained, after purification by column chromatography, in 10% yield (Scheme 2).

Sonogashira reaction protocols have been recently used with success as high-yielding procedures for the macrocyclization step in the formation of shape-persistent cyclic moieties.[13] We intially tested these methods on model substrates with results which essentially reproduced those reported in the literature in terms of isolated yields, at different dilution conditions (down to 5 mM).[13] However, when molecular modules (*R*)-**5** and (*R*)-**7**, suitable for Sonogashira coupling, were subjected to either method for the synthesis of the corresponding macrocycle, under different dilution conditions (down to 5 mM), no product could be isolated and only baseline material could be detected.

Macrocycles bearing shorter diphenyl spacers (Scheme 3) were succesfully synthesized following different routes: Macrocycle (*RR*)-**10**, *via* high dilution macrocyclization (5 mM each reagent) using precursors (*R*)-**1** and 4,4′-bis(bromomethyl)biphenyl under standard Williamson conditions and high dilution (5 mM in each reagent); The synthesis of ester-containing macrocycle (*RR*)-**11** was instead achieved by reacting the diol (*R*)-**1** and equimolar amounts of the acid chloride of [1,1′-biphenyl]-4,4′-dicarboxylic acid, again under high dilution conditions (5 mM for each reagent in $CH_2Cl_2$ with an excess $Et_3N$ as base scavenger).




**Scheme 3** Synthesis of macrocycles bearing short spacers.

The room temperature $^1H$ NMR spectra for all cyclic compounds (*RR*)-**8–11** revealed the presence of only one set of signals for each group of symmetry-related proton resonances, as all possible dynamic processes (conformational inversion of boat and chair-like structures, conformational locking of the aromatic ester residues) are, as expected, fast on the NMR timescale at this temperature. The difference in chemical shift for the two different sets of diastereotopic methylene proton resonances, placed in proximity of either the spacer or the binaphthyl unit, in the case of the ether-bridged macrocycles (*RR*)-**8** and (*RR*)-**10**, is minimal, in both cases these resonances appearing as well defined AB quartets (Fig. S1†). It is interesting to detect rather large differences in the chemical shift of the OMe groups proton resonances (from 3.22 ppm in the case of (*RR*)-**8** to 3.51 ppm in the case of (*RR*)-**11**, Table S1), indicating considerable variability in the internal environments of the covalent cyclic structures as a consequence of the change in the size of the spacing units.

### Spectroscopic and complexation studies

The UV/Vis absorption spectra of the four macrocyclic compounds described in this paper show the major absorption band centered around 230 nm typical of the binaphthyl chromophore, with molar absorption coefficient values within the range of those already reported for this class of absorbers.[14] Other bands, with maxima in the range 250–300 nm for all macrocycles, are consistent with the values reported in the literature for model compounds identical to the spacing units (see Fig. S2†).

Circular dichroism spectroscopy of macrocycles (*RR*)-**8–11** show the exciton couplet typical of binaphthyl moieties (Fig. 2), corresponding to the maximum absorption band in the UV/Vis spectra and related to the $^1$B spectral region of the 2-naphthol chromophore (*ca.* 230 nm for all compounds). No induced CD activity is associated with other absorption bands in the UV/Vis spectra. The intensity of the low energy branch of the couplet has been associated with the dihedral or "bite" angle of the binaphthyl unit, defined by the two naphthyl planes.[14]

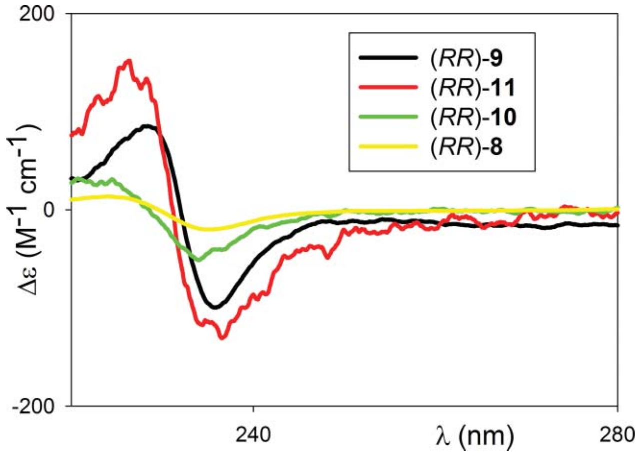



**Fig. 2** CD spectra of macrocycles (*RR*)-**8–11** (concentrations in the range 0.8–1.5 $10^{-6}$ M in EtOH).

The normalized Δε values recorded (−130 for (*RR*)-**11**, −98 for (*RR*)-**9**, −50 for (*RR*)-**10**, −20 for (*RR*)-**8**) demonstrate considerable conformational variability among the four macrocycles. Since compounds (*RR*)-**8–11** possess the same substituent (OMe) in the 2,2′-positions, the differences between the above mentioned values should be ascribed to variations of the average dihedral angle of the binaphthyl units as a consequence of their incorporation into cyclic structures of differing sizes and structural flexibility. This can also be understood as a consequence of moderately intense buttressing effects of the neighbouring 3,3′-positions, as benzylic ether or ester. The substantial differences in the dihedral angles of the binaphthyl units for compounds (*RR*)-**8–11** were also confirmed by molecular modeling (*vide infra*).

The large internal cavities of shape-persistent macrocycles and the exploitation of concave–convex complementarity has resulted in several types of macrocyclic host molecules for $C_{60}$ and other larger fullerenes as guests. Planar aromatic π-electron extended surfaces, suitably positioned within a large covalent macrocyclic framework, have shown to be particularly effective in this context.[15] The observation that the cavities of macrocycles (*RR*)-**8–11** measure between 0.5 and 1 nm in size (*vide infra* molecular modeling), similar to other shape-persistent macrocycles that have already been reported to show recognition properties towards $C_{60}$, prompted us to investigate the complexation tendencies of these large rigid cycles towards $C_{60}$.

Whereas titration of a solution of $C_{60}$ with increasing amounts of macrocycle (*RR*)-**10** in toluene resulted in no detectable changes in the UV/Vis spectra, in the case of macrocyles (*RR*)-**8**, (*RR*)-**9** and (*RR*)-**11**, a variation of the absorption band above 400 nm could be readily detected (Fig. 3 and Fig. S2 and S3†). This band, arising with complex formation, is similar, in terms of shape, to previously reported cases, involving both cyclic π-electron rich and π-electron deficient substrates.[15c,e,j]

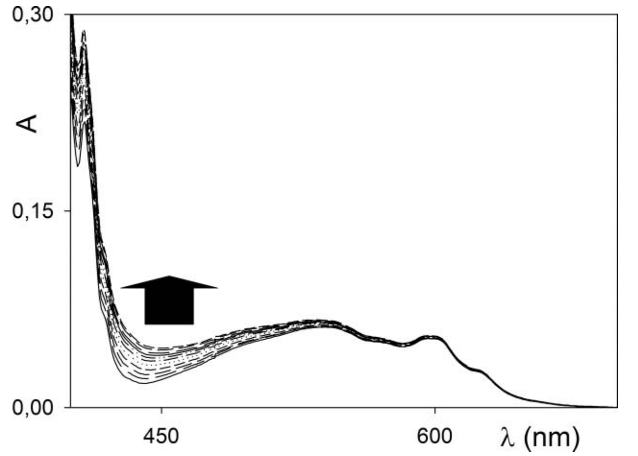



**Fig. 3** Titration of $C_{60}$ (69 μM) with macrocycle (*RR*)-**11** (0–839 μM) in toluene at 25 °C.

The UV-vis absorption spectra of a series of about 10 solutions of ~100 μM $C_{60}$ with varying amounts of macrocycle were used to quantify complexation to $C_{60}$. Individual wavelengths were insufficient for determining the binding constants because the trailing absorbance of the ligands into the visible range obfuscated potential binding curves. Fitting with a 1 : 1 binding isotherm could indeed be carried out with satisfactory regression indexes, but only with large uncertainties regarding the two calculated parameters: the association constant and molar absorptivity of the 1 : 1 complex.[16] In order to adequately delineate these two parameters, the entire set of wavelengths from 400 to 700 nm for each titration were modeled simultaneously using Sivvu™, a non-linear least-squares regression program for performing equilibrium-restricted factor analysis.[17]

In the three cases in which binding was evident, simple 1 : 1 binding proved to be the best model (Sivvu™ permits the user to readily test and evaluate models involving multiple arbitrary chemical reactions). Table 1 lists the fitting results, and Fig. 4 shows the calculated molar absorptivity curves for the 1 : 1 complexes, along with that for $C_{60}$. The molar absorptivity values for the macrocyles were not assumed to be zero, and their calculated values (Fig. S5†) acceptably matched the experimentally verified

**Table 1** Association constant for the 1 : 1 complexes between $C_{60}$ and macrocycles (*RR*)-**8**, (*RR*)-**9** and (*RR*)-**11** measured by UV/Vis titration at 298 K in toluene, and molar absorption coefficient values of the 1 : 1 complexes at two key wavelengths

| Compound | Log $K_a$/ $M^{-1}$ | $\varepsilon_{407}$ [b]/ $M^{-1}cm^{-1}$ | $\varepsilon_{437}$ [b]/ $M^{-1}cm^{-1}$ | RMS Residual[a] | $R^2$ |
|---|---|---|---|---|---|
| (*RR*)-**8** | 3.509(2) | 3015 | 0 | 0.00040 | 99.9997% |
| (*RR*)-**9** | 4.37(2) | 4231 | 592 | 0.00077 | 99.9994% |
| (*RR*)-**11** | 3.498(4) | 2993 | 150 | 0.00022 | 99.9999% |

[a] Root-mean-square of the point-by-point differences between the ~3000 absorbance datum and the calculated values for each set of absorbance curves assuming 1 : 1 binding and the corresponding binding constant. [b] Molar absorption coefficient values of $C_{60}$ at 407 nm = 3200 ($M^{-1}cm^{-1}$) and at 437 nm = 250 ($M^{-1}cm^{-1}$).

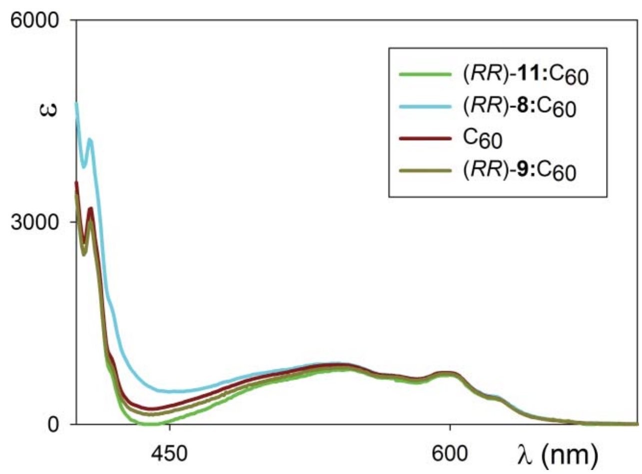



**Fig. 4** Calculated curves for the 1 : 1 complexes between macrocycles (*RR*)-**8**, (*RR*)-**9** and (*RR*)-**11** in toluene at 25 °C.

ones. Indeed, the absorptivity of the 1 : 1 complexes was established to be quite similar, but definitively not identical, to the sum of the molar absorptivity curves for the macrocyle and $C_{60}$ by itself. Models with no binding resulted in RMS Residuals that were 90–140% higher than for those with binding. Note that sufficient macrocycle (5–12 equivalents) was combined with $C_{60}$ to complex at least 65% of it. It is also important to note that the product of the $C_{60}$ concentration and the binding constant is less than 2.5 in all cases, validating the determination of the latter *via* these titration experiments.[18]

From these data, it is clear that macrocycle (*RR*)-**9** binds most strongly. By inspecting the calculated UV/Vis curves for the 1 : 1 complexes (Fig. 4), it is likewise evident how this macrocycle perturbs the $C_{60}$ bands in the region 400–450 nm the most. By studying the UV/Vis spectra of $C_{60}$ in different solvents, previous work has shown how its absorbance in the 400–450 nm region is strongly dependent on the electronic nature and on the π–π stacking interaction abilities of the aromatic solvent involved.[19] Control experiments with fragments of the cyclic structures, such as compound (*R*)-**1**, revealed no measurable shift in the UV/Vis spectrum of $C_{60}$ upon addition of the host.[8b] It is likely that a combination of nonspecific host–guest interactions (such as π–π stacking, Van-der-Waals contacts between the polar -$OCH_3$ groups and the π-surface of the guest, *vide infra*) contribute to the overall stabilization of the complexes.

Since $C_{60}$ is devoid of any chemical handle for direct point recognition, sensing it with CD spectroscopy requires a different strategy from those for ordinary asymmetric compounds. The detection of $C_{60}$ itself by CD spectroscopy by means of an induced CD effect on either the host or the $C_{60}$ guest absorption bands has been reported, to our knowledge, in only very selected cases.[15p,15q] Sensing of $C_{60}$ using CD spectroscopy could in principle be achieved with our macrocycles by means of a detectable variation of the exciton couplet signature of the hosts around 230 nm, which was however not observed in our systems. As binding constants are not extremely high, and molar absorption coefficients of either hosts and guest are high at 230 nm, the usable concentration range was well below 10 μM, pushing the complex towards dissociation. We considered only the 400–700 nm range (Fig. 5), in which the host absorbance (small and tailing off at these wavelengths) and guest absorbance could be maintained below the working range for CD detection even when using excess equivalents of $C_{60}$ to move towards complexation. Indeed, an induced CD effect in the band of $C_{60}$ complex could be seen, only in the case of macrocycle (*RR*)-**8**, indicative of a weak chirality of the supramolecular complex as a whole.[20] This qualitative response corresponds with the calculated absorbance for the complexes (Fig. 4), the 1 : 1 complex (*RR*)-**8** with $C_{60}$ being the most intensely absorbing in the selected region. As a comparison, (*RR*)-**11** in the presence of $C_{60}$, even in more concentrated solutions (Fig. 5), did not give a similar response.

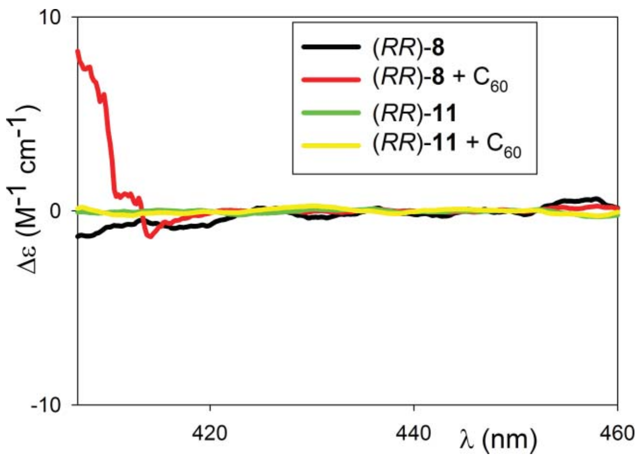



**Fig. 5** CD spectra of macrocycle (*RR*)-**8** (10 μM) with $C_{60}$ (40 μM) and without $C_{60}$ in toluene at 25 °C. CD spectra of the macrocycle (*RR*)-**11** 100 μM) with $C_{60}$ (400 μM) and without $C_{60}$ in toluene at 25 °C for comparison.

## Molecular modeling

Molecular modeling was performed on the structures of compounds (*RR*)-**8**, (*RR*)-**9**, (*RR*)-**10** and (*RR*)-**11** in order to elucidate the main stabilizing interactions for $C_{60}$ and to estimate the final complexation energies. The method used for all the calculations was a semiempirical PM3 method.[21] Several conformers for each of the macrocyclic structures were obtained by preliminary optimization, and they were then subjected to further refinement by molecular dynamics and subsequent reoptimization. The most stable minimized structures of the macrocycles are shown in the Supporting Information (Fig. S9†). Macrocycles (*RR*)-**8** and (*RR*)-**9** (long spacers) possess a distorted molecular conformation in which one $C_2$ axis (the one perpendicular to the mean plane of macrocycle) is maintained. The most stable conformers are at least 5 kcal mol$^{-1}$ lower in energies with respect to all the other studied conformer. The distance between the conjugated spacers (measured as the shortest distance between acetylene carbon atoms) is 0.97 nm in the case of (*RR*)-**8**, but in the case of (*RR*)-**9** the two conjugated spacers are parallel and significantly offset, resulting in a reduction of the dimensions of the internal cavity to 0.65 nm. The dihedral angle defined by the symmetry related binaphthyl units is 85° in both macrocycles. The conjugated spacers are slightly bent in the case of macrocycle (*RR*)-**9** (the angle between the carbon atoms at the edges and at the center of the spacer is 10°), whereas the spacers of (*RR*)-**8** do not show any significant deviation from planarity.

Both macrocycles (*RR*)-**10** and (*RR*)-**11** (short spacers) show a complete loss of the $D_2$ molecular symmetry in their most stable conformation. The ether linkages in macrocycle (*RR*)-**10**, as compared to the ester linkages of macrocycle (*RR*)-**11**, allow more flexibility of the spacers, which severely twist with respect to eachother to greatly reduce the molecular cavity (the closest contact between carbon atoms of the two neighbouring spacing units being 0.36 nm) and preserving almost exactly one $C_2$ axis. The dihedral angle of the binaphthyl units is between 97° and 103° in both macrocycles.

The geometry of the 1 : 1 complexes with minimal energy are shown in Fig. 6. In the cases of (*RR*)-**8** and (*RR*)-**9**, the minimized structures of these complexes are calculated to be *ca.* 1 kcal mol$^{-1}$ more stable than the minimized macrocycles alone. Upon complexation, the geometry of the macrocycles does not essentially change. In both cases, the fullerene sits on top of the mean plane of the macrocycles, near the two methoxy functionalities of the binaphthyl units (closest contact between the $OCH_3$ carbon atoms and $C_{60}$ carbons are 0.36 nm in both cases). The closest contacts between the acetylene carbon atoms and $C_{60}$ carbons are 0.43 nm in the case of (*RR*)-**8**. In the case of (*RR*)-**9**, the offset of the conjugated spacers brings the $C_{60}$ near to a phenyl ring of each spacers (closest contact is 0.36 nm).

In the case of (*RR*)-**11**, the $C_{60}$ is placed alongside with respect to the mean plane of the macrocycle, essentially interacting with the two methoxy functionalities belonging to each of the binaphthyl units across from each other (closest contacts between the $OCH_3$ carbon atoms and $C_{60}$ carbons are 0.57 nm), and with one phenyl ring of one biphenyl moiety (closest contact 0.36 nm). The complexation energy is however sensibly reduced, to a value of 0.5 kcal mol$^{-1}$. Moreover, (*RR*)-**11** possess a high molecular flexibility since different conformers in an energy span of 1–1.5 kcal mol$^{-1}$ could be located. Since the most stable conformer possesses the highest complexation energy, the flexibility could somewhat contribute to decrease entropically the calculated complexation energy.

## Conclusion

The synthesis and characterization of a class of large chiral macrocyclic receptors incorporating axially-chiral binaphthyl units has been accomplished. The introduction of ester or ether functionalities ensure the required degree of flexibility and chemical inertness, making these substrates, if of suitable size, capable of recognizing base-degradable, convex substrates such as $C_{60}$. The binding strengths depend on the lengths of the spacing units, as well as their electronic properties. The binding constants could be determined with a high degree of accuracy *via* equilibrium-restricted factor analysis. A suitable combination of stabilizing functionalities, as in the case of (*RR*)-**8**, demonstrate the possibility of transferring chirality to the supramolecular complex. We are currently designing systems in which the CD detection of $C_{60}$ and related fullerene guests could be more strongly addressed.

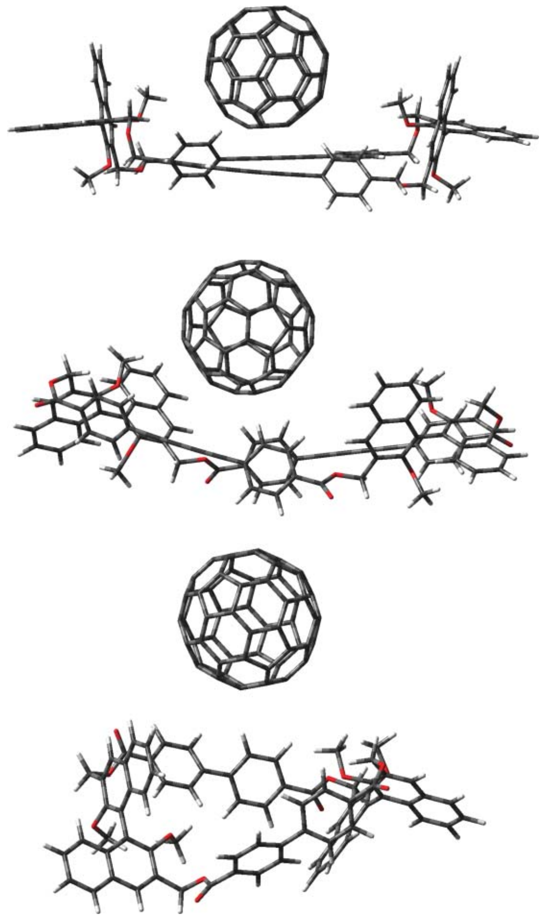


**Fig. 6** View for the calculated minima for the 1 : 1 complexes $C_{60}$ : (*RR*)-**8** (top), $C_{60}$ : (*RR*)-**9** (middle), and $C_{60}$ : (*RR*)-**11** (bottom).

## Experimental

### General experimental

All commercially available compounds were purchased from commercial sources and used as received. Compounds 4-dimethylaminopyridiunium *p*-toluenesulfonate (DPTSA),[11a] (*R*)-**1**,[9] 4,4′-bis(bromomethyl)biphenyl[22] were prepared according to literature procedures. THF (Na) and $CH_2Cl_2$ ($CaH_2$) were dried before use. Analytical thin layer chromatography was performed on silica gel, chromophore loaded, commercially available plates. Flash chromatography was carried out using silica gel (pore size 60 Å, 230–400 mesh). $^1$H and $^{13}$C NMR spectra were recorded from solutions in $CDCl_3$ on 200 or 300 MHz spectrometer with the solvent residual proton signal or tetramethylsilane as a standard. The UV/Vis spectroscopic studies were recorded using commercially-available spectrophotometers. Mass spectra were recorded using an electrospray ionization instrument. Optical rotations were measured on a polarimeter with a sodium lamp ($\lambda$ = 589 nm) and are reported as follows: $[\alpha]_D^{25}$ ($c = g$ (100 mL)$^{-1}$, solvent). CD spectroscopy was performed using a spectropolarimeter; spectra were recorded at 25 °C at a scanning speed of 50 nm min $^{-1}$ and were background corrected.

### Compound 3

$PdCl_2(PPh_3)_2$ (58 mg, 0.082 mmol) and CuI (16 mg, 0.082 mmol) were charged in a flask, dried *in vacuo* under nitrogen and dry THF (5 mL), $Et_3N$ (624 mg, 6.16 mmol) and methyl 4-iodobenzoate (1 g, 3.82 mmol) were added. After 10 min of stirring at room temperature, a solution of trimethilsylilacetylene (408 mg, 4.16 mmol) in dry THF (7 mL) was added. After further stirring for 20 h at room temperature, $H_2O$ (50 mL) was added to the reaction mixture and the aqueous layer was extracted with $Et_2O$ (3 × 50 mL) and dried ($Na_2SO_4$). The solution was filtered and concentrated *in vacuo*, and the crude product was purified by column chromatography ($SiO_2$; hexanes/$CH_2Cl_2$: 99/1 to 9/1) to yield *methyl 4-[(trimethylsilyl)ethynyl]benzoate* (735 mg, 83%). The $^1$H NMR spectrum was fully consistent with that reported in the literature.[23] $K_2CO_3$ (44 mg, 0.317 mmol) was added to a solution of *methyl 4-[(trimethylsilyl)ethynyl]benzoate* (735 mg, 3.17 mmol) in $CH_2Cl_2$ (18 mL) and MeOH (30 mL). The solution was degassed and stirred under nitrogen at room temperature for 5 h. The reaction solvent was removed *in vacuo* and purification by column chromatography ($SiO_2$; hexanes/AcOEt: 9/1) afforded **3** (431 mg, 85%). The $^1$H NMR spectrum was fully consistent with that reported in the literature.[24]

### Compound (*R*)-4

(*R*)-**1** (153 mg, 0.41 mmol) was added to a solution of NaH (30 mg, 1.02 mmol) in dry THF (9 mL) and the suspension was brought at reflux under nitrogen and stirring. After 10 min a solution of **2** (159 mg, 0.815 mmol) in dry THF (9 mL) was added dropwise. After stirring at reflux for 15 h, the reaction mixture was warmed at room temperature and quenched with $H_2O$. THF was removed *in vacuo*, and the aqueous layer was extracted with AcOEt (3 × 30 mL) and dried ($Na_2SO_4$). The crude product was purified by column chromatography ($SiO_2$; hexanes/AcOEt: 9/1) to yield (*R*)-**4** as a white solid (135 mg, 55%). $[\alpha]_D^{25}$ +48 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.15 (s, 2H; binaphthyl), 7.95 (d, 2H; binaphthyl), 7.49 (m, 10H; binaphthyl and phenyl), 7.26 (q, 4H; binaphthyl), 4.91 (q, 4H; binaphthyl -$CH_2$O-), 4.78 (s, 4H; Ar-$CH_2$O-), 3.31 (s, 6H; -$OCH_3$), 3.12 (s, 2H; alkyne). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 154.8 (Cq-OMe), 139.1 (Cq), 133.8 (Cq), 132.1 (CH), 131.4 (Cq), 130.4 (Cq), 128.9 (CH), 128.0 (CH), 127.5 (2CH), 126.3 (CH), 125.6 (CH), 124.8 (CH), 124.3 (Cq), 121.3 (Cq), 83.4 (Cq alkyne), 77.1 (Cq alkyne), 72.3 ($CH_2$), 68.2 ($CH_2$), 61.0 (OMe). MS(ESI): *m/z* (%): 625.1 ([*M* + Na]$^+$, 100). Found: C, 83.4; H, 6.0. Calc. for $C_{42}H_{34}O_4$: C, 83.7; H, 5.7. $\lambda_{max}$(EtOH)/nm 235 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 19 200), 262 (15 800).

### Compound (*R*)-5

A solution of (*R*)-**1** (139 mg, 0.37 mmol) in dry $CH_2Cl_2$ (10 mL) and a solution of **3** (120 mg, 0.82 mmol) in dry $CH_2Cl_2$ (7.5 mL) were added to a flask with DPTSA (231 mg, 0.74 mmol) under nitrogen. After stirring for 10 min, *N*,*N*′-diisopropylcarbodiimide (263 mg, 2.09 mmol) was added and the suspension gradually became homogeneous during the course of a few hours. After stirring for 15 h, the reaction mixture was quenched with a solution of 3 N HCl (until acidity) and the aqueous layer was extracted with $Et_2O$ (3 × 25 mL) and dried ($Na_2SO_4$). The solution was filtered, the solvent removed *in vacuo* and the crude product was purified by column chromatography ($SiO_2$; hexanes/AcOEt: 95/5) to yield (*R*)-**5** as a white solid (170 mg, 73%). $[\alpha]_D^{25}$ +89 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.13 (s, 2H; binaphthyl), 8.12 (d, 4H; phenyl), 7.93 (d, 2H; binaphthyl), 7.58 (d, 4H; phenyl), 7.45 (t, 2H; binaphthyl), 7.30 (m, 4H; binaphthyl), 5.72 (q, 4H; binaphthyl-C*H*$_2$O-), 3.38 (s, 6H; -$OCH_3$), 3.26 (s, 2H; alkyne). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 165.6 (C=O), 154.8 (*Cq*-OMe), 134.2 (Cq), 132.1 (2CH), 130.3 (Cq), 130.0 (CH), 129.5 (2CH), 129.2 (2Cq), 128.1 (CH), 126.8 (CH+Cq), 125.6 (CH), 125.1 (CH), 124.4 (Cq), 82.7 (CH), 80.1 (Cq alkyne), 63.0 ($CH_2$), 61.2 (OMe). Found: C, 80.2; H, 5.0. Calc. for $C_{42}H_{30}O_6$: C, 80.0; H, 4.8. $\lambda_{max}$(EtOH)/nm 228 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 175 200), 259 (76 100).

### Compound (*R*)-6

(*R*)-**1** (202 mg, 0.50 mmol) was added to a solution of NaH (85 mg, 1.35 mmol) in dry THF (10 mL) and the suspension was brought at reflux under nitrogen and stirring. After 10 min a solution of 4-iodobenzyl bromide **2a** (202 mg, 1.08 mmol) in dry THF (10 mL) was added dropwise. After stirring at reflux for 15 h, the reaction mixture was warmed at room temperature and quenched with $H_2O$. THF was removed *in vacuo*, and the aqueous layer was extracted with AcOEt (3 × 30 mL) and dried ($Na_2SO_4$). The crude product was purified by column chromatography ($SiO_2$; hexanes/AcOEt: 95/5) to yield (*R*)-**6** as a white solid (191 mg, 64%). $[\alpha]_D^{25}$ +79 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.22 (s, 2H; binaphthyl), 8.02 (d, 2H; binaphthyl), 7.50-7.29 (m, 16H; phenyl and binaphthyl), 4.98 (q, 4H; Binaphthyl-C*H*$_2$O-), 4.85 (s, 4H; Ar–C*H*$_2$O-), 3.38 (s, 6H; -$OCH_3$). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 154.6 (*Cq*-OMe), 138.1 (Cq), 133.8 (Cq), 131.6 (Cq), 130.5 (Cq), 128.9 (CH), 128.4 (2CH), 128.0 (CH), 127.8 (2CH), 127.6 (CH), 126.2 (CH), 125.6 (CH), 124.7 (CH), 124.3 (Cq), 72.9 ($CH_2$), 68.0 ($CH_2$), 61.0 (OMe). Found: C, 82.2; H, 6.0. Calc. for $C_{38}H_{34}O_4$: C, 82.3; H, 6.2. $\lambda_{max}$(EtOH)/nm 231 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 112 500), 284 (12 300).

### Compound (*R*)-7

A solution of (*R*)-**1** (139 mg, 0.37 mmol) in dry $CH_2Cl_2$ (10 mL) and a solution of 4-iodobenzoic acid **3a** (183 mg, 0.74 mmol) in dry $CH_2Cl_2$ (7.5 mL) were added to a flask with DPTSA (231 mg, 0.74 mmol) under nitrogen. After stirring for 10 min, *N*,*N*′-diisopropylcarbodiimide (263 mg, 2.09 mmol) was added and the suspension gradually became homogeneous during the course of a few hours. After stirring for 15 h, the reaction mixture was quenched with a solution of 3 N HCl (until acidity) and the aqueous layer was extracted with $Et_2O$ (3 × 25 mL) and dried ($Na_2SO_4$). The solution was filtered, the solvent removed *in vacuo* and the crude product was purified by column chromatography ($SiO_2$; hexanes/AcOEt: 95/5) to yield (*R*)-**7** as a white solid

(207 mg, 67%). $[\alpha]_D^{25}$ +102 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.11 (s, 2H; binaphthyl), 7.93 (d, 2H; binaphthyl), 7.85 (s, 8H; phenyl), 7.46 (t, 2H; binaphthyl), 7.26 (q, 4H; binaphthyl), 5.69 (q, 4H; binaphthyl-C$H_2$O-), 3.36 (s, 6H; -$OCH_3$). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 165.8 (*C*=O), 154.8 (*Cq*-OMe), 137.7 (2CH), 134.2 (Cq), 131.0 (2CH), 130.2 (Cq), 130.0 (CH), 129.6 (Cq), 129.5 (Cq), 129.1 (Cq), 128.1 (CH), 126.8 (CH), 125.6 (CH), 125.0 (CH), 124.4 (Cq), 100.8 (Cq-I), 63.0 ($CH_2$), 61.2 (OMe). Found: C, 55.0; H, 3.6. Calc. for $C_{38}H_{28}I_2O_6$: C, 54.7; H, 3.4. $\lambda_{max}$(EtOH)/nm 230 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 41 100).

### Macrocycle (*RR*)-8

A solution of (*R*)-**4** (500 mg, 0.83 mmol) and CuCl (5.55 g, 56.1 mmol) in $CH_2Cl_2$ (1200 mL) was vigorously stirred under $O_2$ for 20 min. Then *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (6.75 g, 58.1 mmol) was added and the solution was stirred at room temperature for 36 h. The reaction mixture was quenched with $H_2O$, the green organic layer was washed with $H_2O$ until all the copper blue salts were transferred in the aqueous layer. The organic layer was then dried ($Na_2SO_4$), filtered, the solvent removed *in vacuo* and the crude product purified by column chromatography ($SiO_2$; hexanes/AcOEt: 9/1) to yield (*RR*)-**8** as a white solid (50 mg, 10%). $[\alpha]_D^{25}$ +145 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.13 (s, 4H; binaphthyl), 7.95 (d, 4H; binaphthyl), 7.30 (m, 28H; binaphthyl and phenyl), 4.76 (2q, 16H; C$H_2$-O–C$H_2$), 3.22 (s, 12H; -$OCH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 154.7 (*Cq*-OMe), 139.4 (Cq), 133.9 (Cq), 132.5 (2CH), 131.3 (Cq), 130.4 (Cq), 129.5 (CH), 128.0 (CH), 127.9 (2CH), 126.3 (CH), 125.6 (CH), 124.8 (CH), 124.3 (Cq), 121.0 (Cq), 81.3 (Cq-alkyne), 73.9 (Cq-alkyne), 72.2 ($CH_2$), 67.7 ($CH_2$), 61.0 (OMe). MS(ESI): *m*/*z* (%): 1223.6 ([*M* + Na]$^+$, 100). Found: C, 84.3; H, 5.4. Calc. for $C_{84}H_{64}O_8$: C, 84.0; H, 5.4. $\lambda_{max}$(EtOH)/nm 231 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 58 300), 268 (40 600), 312 (15 300).

### Macrocycle (*RR*)-9

A solution of (*R*)-**5** (250 mg, 0.40 mmol) and CuCl (2.65 g, 26.8 mmol) in $CH_2Cl_2$ (500 mL) was vigorously stirred under $O_2$ for 20 min. Then *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (3.23 g, 27.8 mmol) was added and the solution was stirred at room temperature for 36 h. The reaction mixture was quenched with $H_2O$, the green organic layer was washed with $H_2O$ until all the copper blue salts were transferred in the aqueous layer. The organic layer was then dried ($Na_2SO_4$), filtered, the solvent removed *in vacuo* and the crude product purified by column chromatography ($SiO_2$; hexanes/AcOEt: 9/1) to yield (*RR*)-**8** as a white-yellow solid (25 mg, 10%). $[\alpha]_D^{25}$ +169 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.05 (m, 16H; binaphthyl and phenyl), 7.40 (m, 20H; binaphthyl and phenyl), 5.62 (dd, 8H; binaphthyl-C$H_2$O-), 3.47 (s, 12H; -$OCH_3$). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 165.4 (*C*=O), 155.6 (*Cq*-OMe), 134.6 (Cq), 132.7 (CH), 132.3 (2CH), 130.5 (Cq), 130.2 (Cq), 129.4 (2CH), 128.6 (Cq), 128.1 (CH), 127.0 (CH), 126.1 (Cq), 125.5 (CH), 125.2 (CH), 125.1 (Cq), 81.7 (Cq-alkyne), 77.9 (Cq-alkyne), 64.4 ($CH_2$), 61.4 (OMe). MS(ESI): *m*/*z* (%): 1279.3 ([*M* + Na]$^+$, 100). Found: C, 80.3; H, 4.4. Calc. for $C_{84}H_{56}O_{12}$: C, 80.3; H. 4.5. $\lambda_{max}$(EtOH)/nm 231 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 60 700), 270 (57 700).

### Macrocycle (*RR*)-10

A solution of compound (*R*)-**1** (310 mg, 0.83 mmol) and 4,4′-di(bromomethyl)biphenyl (282 mg, 0.83 mmol) in THF (85 mL) was added to a refluxing solution of NaH (50 mg, 2.07 mmol) in THF (85 mL). After 15 h under reflux and magnetic stirring, the solution was cooled at 0 °C and $H_2O$ was added. After warming at room temperature, THF was evaporated and the aqueous solution was extracted with $CH_2Cl_2$. The organic layers were dried ($Na_2SO_4$), the solvent removed *in vacuo* and the product purified by column chromatography ($SiO_2$; hexanes/AcOEt: 8/2 and then $CH_2Cl_2$–hexane: 1/1) to yield (*RR*)-**10** as a white solid (60 mg, 17%). $[\alpha]_D^{25}$ +105 (*c* 0.005 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.15 (s, 4H; binaphthyl), 7.93 (d, 4H; binaphthyl), 7.52 (d, 8H; phenyl), 7.42 (d, 8H; phenyl), 7.40 (t, 4H; binaphtyl), 7.25 (t, 4H; binaphthyl), 7.17 (d, 4H; binaphthyl), 4.72–4.95 (m, 16H; -C$H_2$OC$H_2$-), 3.24 (s, 12H; OMe). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 154.7 (Cq), 140.2 (Cq), 136.9 (Cq), 133.8 Cq), 131.6 (Cq), 130.5 (Cq), 129.3 (CH), 128.5 (CH), 128.0 (CH), 127.0 (CH), 126.2 (CH), 125.6 (CH), 124.7 (CH), 124.3 (Cq), 72.5 (-OC$H_2$-), 67.4 (-C$H_2$O-), 61.1 (OMe). MS(ESI): *m*/*z* (%): 1127.7 ([*M* + Na]$^+$, 100). Found: C, 82.3; H, 5.6. Calc. for $C_{76}H_{64}O_8$: C, 82.6; H, 5.8. $\lambda_{max}$(EtOH)/nm 230 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 69 700), 270 (34 500).

### Macrocycle (*RR*)-11

Biphenyl-4,4′-dicarboxylic acid (0.2 mmol, 116 mg) was added to a solution of $SOCl_2$ (6 mL) and DMF (1 mL). After 15 h of magnetic stirring and refluxing, the solution was cooled and the solvents were evaporated. The resulting solid (biphenyl-4,4′-dicarbonyl dichloride) was dissolved in dry $CH_2Cl_2$ (10 mL); this solution, and a solution of compound (*R*)-**1** (74.8 mg, 0.2 mmol) in dry $CH_2Cl_2$ (10 mL) were added simultaneously and dropwise to a solution of $Et_3N$ (40 mg, 0.4 mmol), DMAP (2.4 mg, 0.2 mmol) in $CH_2Cl_2$ (10 mL). After 24 h of magnetic stirring at room temperature, the solution was refluxed for 2 h, then $H_2O$ was added and the organic layers were dried ($Na_2SO_4$). Flash chromatography ($SiO_2$; hexanes/AcOEt: 8/2) afforded pure compound (*RR*)-**11** (10 mg, 10%). $[\alpha]_D^{25}$ +147 (*c* 0.001 in $CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ = 8.16 (s, 4H; binaphthyl), 8.06 (d, 8H; phenyl), 7.95 (d, 4H; binaphthyl), 7.48 (d, 8H; *J* = 4 Hz, phenyl), 7.46 (m, 4H; binaphthyl), 7.32 (m, 4H; binaphthyl), 7.18 (m, 4H; binaphtyl), 5.79 (d, 4H; -C$H_2$OCO-), 5.44 (d, 4H; -C$H_2$OCO-), 3.50 (s, 12H; -$OCH_3$). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) $\delta$ = 166.0 (C=O), 155.8 (Cq), 144.1 (Cq), 134.7 (Cq), 132.8 (CH), 130.2 (Cq), 130.0 (CH), 129.6 (Cq), 128.7 (Cq), 128.2 (CH), 127.1 (CH), 125.5 (CH), 125.2 (CH), 124.9 (Cq), 124.7 (Cq), 118.6 (CH), 77.1 (Cq), 64.2 ($CH_2$), 61.5 (OMe). MS(ESI): *m*/*z* (%): 1183.6 ([*M* + Na]$^+$, 100). Found: C, 78.9; H, 5.0. Calc. for $C_{76}H_{56}O_{12}$: C, 78.6; H, 4.9. $\lambda_{max}$(EtOH)/nm 230 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 73 500), 283 (25 300).

### UV/Vis titrations

Toluene (UV/Vis spectroscopic grade) was used. An analytical balance (with a precision of $10^{-4}$ g) was used to weigh the samples for the stock solutions. Aliquots of these stock solutions were then taken via high precision pipettes to prepare the cuvette samples for spectrophotometric analyses. The titration experiments were conducted as follows: to a stock solution of $C_{60}$ (solution A) in toluene, were added several aliquots of the host (solution B). Solution B is formed by the ligand at higher concentration dissolved in solution A, in order to maintain the guest always at the same, constant concentration.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