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ON/OFF metal-triggered molecular tweezers for fullerene recognition

New molecular tweezers for fullerene recognition based on bipyridine-corannulene motifs have been obtained. Reversible and quantitative switching ON/OFF state is achieved by metal coordination, allowing the control of the fullerene recognition capability and leading to the formation of an effective metal-triggered molecular machine.

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Cite this: *Chem. Commun.*, 2021, 57, 11013

Received 28th June 2021,
Accepted 13th September 2021

DOI: 10.1039/d1cc03451k

rsc.li/chemcomm

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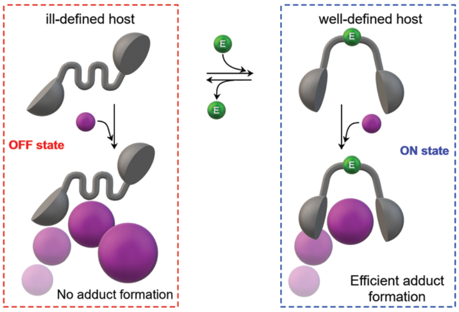
Herein, we report molecular tweezers for fullerene recognition based on 2,2′-bipyridine-bearing corannulene motifs. The *syn* or *anti* confirmation can be selected simply by Cu(I) coordination/decoordination, thus controlling the fullerene recognition capability of the system on demand and leading to the formation of effective metal-triggered ON/OFF molecular tweezers.

Stimuli-responsive artificial materials are synthetic multistable systems capable of carrying out a macroscopic task after stimulation-induced structure changes of their components at the microscopic level.[1] Most of these architectures have been designed using mechanisms occurring in biological species as blueprints (*i.e.*, bioinspired design)[2] and mimic natural processes such as the allosteric behaviour promoted by chemical effectors in enzymes, for instance.[3] One interesting approach is the usage of coordination complex chemistry, which encompasses a vast assortment of transition metals whose ability to bind multiple ligands with a wide range of affinities allows the formation of complex systems.[4] Such affinities can be modulated and utilized in coordination–decoordination schemes that ultimately modify their structure, giving rise to metal-based responsive architectures that act as molecular machines.[5] Among the various possible applications, fullerene recognition is one of the most popular, as evidenced by the literature regarding the construction of discrete coordination cages.[6] These motifs rely on the self-assembly of the corresponding subunits to furnish a shape-persistent molecular cage with the appropriate cavity size to host a fullerene and stabilize the inclusion complex through multiple attractive supramolecular interactions. In most cases, a stimulus capable of cleaving the metal–ligand bonds disassembles the cage to release the guest. Another simpler approach could be the synthesis of switchable molecular tweezers in which the coordination (or decoordination) event triggers a crucial conformational change of the ligand that forms (or disrupts) an optimal cavity for fullerene recognition. An appropriately functionalized 2,2′-bipyridine (bpy)[7] should be able to work in this way, taking advantage of the properties of bpy structures as ligands and the possibility of *syn–anti* conformational switching.[8] Some examples utilizing this approach with calix[5]arene[9] or porphyrin[10] clefts have been reported. However, these examples exhibited some issues: (1) the low stability of the coordination complexes, (2) incomplete reversibility of the system and (3) the lack of ON/OFF behaviour (*i.e.*, the fullerene recognition is always active or "ON", although it is modulated by the metal), a phenomenon that we also observed in a previous study using azobenzene-derived photoswitchable hosts.[11] We envisaged the possibility of designing a supramolecular tweezer bearing two corannulene[12] moieties whose conformation would be controlled by a chemical effector, allowing it to be "turned ON" to recognize fullerene in a rigid and well-defined host, and "turned OFF" by scavenging the effector to give an ill-defined host without a suitable cavity to interact with fullerenes (Scheme 1). Corannulene-based hosts have been demonstrated to provide good performance in fullerene recognition in molecular tweezers,[13] molecular clips with multiple units,[14] molecular clips with an active tether[15] and polymers[16] due to the excellent concave–convex complementarity[17]



Scheme 1 Operational principle of reversible bistable molecular tweezers for fullerene recognition controlled by a chemical effector (*E*).

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, full characterization, *in situ* coordination/decoordination cyclic process description and association constant measurements as well as computational calculation details. See DOI: 10.1039/d1cc03451k

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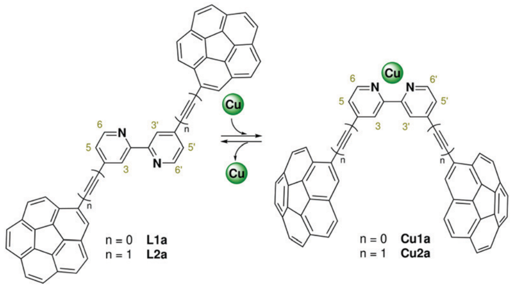

Scheme 2 Chemical structures of compounds **L1a** and **L2a**, whose conformational switching process is governed by a Cu(I) effector.

between the two species. In this work, to combine the interesting properties of readily available simple bidentate-chelating bpy ligands with the convenient curved topology of corannulene, we designed ligands **L1a** and **L2a** (Scheme 2). Our ligand design is based on the following requirements: (1) in the absence of the chemical effector, the system should lack a defined cavity for fullerene recognition (*i.e.*, a noncoordinated or OFF state). We reasoned that a bipyridine framework ligand could meet these requirements, since free bipyridines are known to prefer the *anti* geometry due to steric hinderance between the 3 and 3′ protons (ESI†).[8a] In this case, the absence of a defined cavity for fullerene recognition should disfavour the formation of a supramolecular adduct. (2) The addition of an effector should trigger the formation of a suitable cavity for fullerene recognition (*i.e.*, an ON state). In this work we selected Cu(I) as the effector, which coordinates to the ligands to give the chelate complexes **Cu1a** and **Cu2a**, enabling the selection of the *syn* conformer. Both corannulene subunits are oriented on the same side, creating a preorganized cavity ready for fullerene recognition. More importantly, this process could be reversible, as the two conformers could be interconverted by scavenging the effector from the ON state to release the free ligand, which would relax towards the preferred *anti* conformation, and therefore disrupt the inclusion complex, completing the cycle. As a proof of concept, we present here two models: compound **L1a**, in which the corannulene units are directly connected to the bpy hinge through a C–C bond at positions 4 and 4′, and compound **L2a**, which bears an alkynyl spacer group that confers a larger distance between the two corannulene groups. The resulting cavity in complex **Cu2a** would be larger than the one exhibited by complex **Cu1a**. This feature might impact its ability to recognize fullerenes depending on the overall flexibility and adaptability of the host. The preparation of tweezers **L1a** and **L2a** was carried out by means of Suzuki–Miyaura[18] and Sonogashira[19] C–C cross coupling reactions under microwave irradiation, using 4,4′-dibromo-2,2′-bipyridine as the common starting material and either 1-bromocorannulene or 1-ethynylcorannulene as the functionalized curved polycyclic aromatic hydrocarbon. The subsequent complexes **Cu1a** and **Cu2a** are easily obtained quantitatively by the addition of $[Cu(NCMe)_4]BF_4$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) (ESI†). The choice of this secondary ligand to complete the coordination sphere of Cu(I) was based on its well-known stability, ease of removal (see below) and mild fingerprint for ^{1}H-NMR studies.[20] The final compounds were fully characterized using 1D and 2D NMR measurements, UV-Vis and emission spectroscopy, cyclic voltammetry and high-resolution mass spectrometry (ESI†). The first aspect we tested was the reversibility of the process, *i.e.*, a smooth decoordination/coordination protocol. Metal scavenging in Cu(I) complexes is typically carried out by the addition of an aqueous solution of ammonia or excess of KCN to furnish the corresponding water-soluble complexes, which can be separated from the resulting free bpy by extraction.[21] However, this method requires an additional purification step, precluding our aim of developing an *in situ* switching process. In fact, attempts to apply these protocols *in situ* (conducting the reaction in the NMR tube without a purification step) were unsuccessful because (1) the presence of paramagnetic Cu(II) species prevented NMR analysis and (2) a large excess of the reactant was needed. To circumvent these issues, we developed an alternative method by using the ligand dppe itself as the scavenging agent, which allows *in situ* monitoring of the whole cyclic operation using ^{1}H-NMR. The addition of 1 equiv. of dppe to complexes **Cu1a** or **Cu2a** releases ligand **L1a** or **L2a** to give the more stable homoleptic complex $[Cu(dppe)_2]BF_4$ as a byproduct that remains in solution. In the case of complex **Cu1a**, for instance, protons H^3 and H^6 (red and green in Fig. 1) exhibit significant downfield shifts of 0.12 and 0.27 ppm upon ligand decoordination, respectively, whereas proton H^5 (blue in Fig. 1) is shifted upfield by 0.16 ppm. The chemical shifts of corannulene were also impacted upon coordination. The starting complex **Cu1a** can easily be restored by the addition of 0.5 equiv. of $[Cu(NCMe)_4]BF_4$, which is sufficient to produce heteroleptic **Cu1a** by ligand scrambling, as evidenced by the changes in the chemical shifts of the relevant bpy protons (H^3, H^5 and H^6) as shown in Fig. 1 (ESI†). This straightforward one-pot approach can be applied for a large number of cycles, making it virtually infinitely applicable.§ As noted earlier, **L1a** and **L2a** prefer the *anti* conformation, whereas complexes **Cu1a** and **Cu2a** adopt a *syn* geometry. Thus, our simple approach allows excellent control over the population of both states.

Another advantage of our system is the chemical stability of the involved species, as they do not exhibit interconversion when allowed to stand at room temperature for two weeks. Having harnessed the behaviour of these systems in terms of conformational control, we moved on to study their capability towards fullerene recognition. To do so, fullerenes C_{60} and C_{70} were added to independent solutions of free ligands **L1a** and

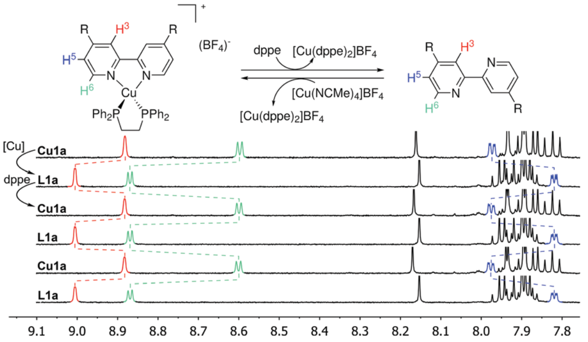

Fig. 1 *In situ* coordination/decoordination process in bpy-derived molecular tweezers along with stacked ^{1}H-NMR spectra of complex **Cu1a** during three switching cycles in CD_2Cl_2 at 298 K.

L2a in CD_2Cl_2 at 298 K. This solvent was chosen over other more common aromatic solvents, such as toluene or chlorobenzene, for stability reasons as the resulting Cu(I) complexes showed evidence of decoordination after 10 minutes in those solvents. Given that both ligands prefer the *anti* conformation and possess freedom of motion, neither formed a cavity between their two corannulene units to host a fullerene (*i.e.*, they were ill-defined hosts); therefore, no supramolecular interaction was observed and the chemical shifts did not change (spectra a and b in Fig. 2). This result is important, since it clearly indicates that the system was in an OFF state as a result of the inability of the free ligands to host fullerene. Complexes **Cu1a** and **Cu2a** were tested using the same protocol. In these cases, remarkable changes in the chemical shifts of some of the protons were observed. As an example, spectra c and d in Fig. 2 highlight the changes in hydrogens H^3 and H^6 for the couple **Cu1a/C$_{70}$**. Proton H^3 (red in Fig. 2) was shifted upfield by 0.073 ppm, whereas proton H^6 (green in Fig. 2) exhibited a downfield shift of 0.011 ppm. The signals of corannulene were also affected (Fig. S79–S90, ESI†). This behaviour clearly demonstrates the existence of an association between the complexes and the fullerenes, as an efficient preorganized cavity has been built between the two corannulene subunits, which effectively encloses the fullerenes due to the excellent concave–convex surface complementarity¶ (*i.e.*, they are well-defined hosts) with an imposed *syn* conformation by Cu(I). In other words, the system is in the ON state. Afterwards, additional cycles of decoordination/coordination were carried out, demonstrating the reversibility of the effector-induced ON/OFF transitions of the molecular tweezers (Fig. 2) (ESI†). To quantify the recognition capability of the reported hosts for the fullerenes, we carried out ^{1}H-NMR titrations in CD_2Cl_2 at 298 K, which gave estimated association constants (K_a) of $(2.00 \pm 0.01) \times 10^3$ M^{-1} and $(4.99 \pm 0.01) \times 10^4$ M^{-1} for complex **Cu1a** with C_{60} and C_{70}, respectively (Fig. 3). For compound **Cu2a**, the obtained K_a values were $(1.15 \pm 0.01) \times 10^3$ M^{-1} for C_{60} and $(2.11 \pm 0.01) \times 10^4$ M^{-1} for C_{70}. The reported values were fitted according to a 1 : 1 stoichiometry model (ESI†). In light of these results, two conclusions were drawn: (1) the binding affinity of the complexes towards C_{70} are one order of magnitude higher than those towards C_{60}, in accordance with the preference for C_{70} previously observed for some corannulene-based molecular tweezers,[13a,c] and (2) the longer ethynyl spacer in **Cu2a** does not dramatically modify the recognition capabilities of the host despite the fact that its cavity is expected to be larger, which could possibly weaken the dispersion and π–π stacking forces. This demonstrates the adaptability of this fairly rigid receptor suggesting that the host and guest interact in an extremely similar way in which fullerene maximizes the approach to the bpy tether. We attempted to further characterize the resulting supramolecular adducts using UV-Vis absorption experiments (Fig. S71, ESI†). Unfortunately, the new charge-transfer band, which was expected to appear at around $\lambda_{abs} \geq 500$ nm,[22] could not be observed. This suggests that this band might be very weak, because (1) the HOMO in the inclusion complex is metal-centred, unlike in the free ligand, where there is a substantial contribution at both corannulene units, (Fig. S103, ESI†), (2) bpy orbitals are normally stabilized (*i.e.*, lower in energy) upon metal coordination, and (3) dispersion forces could play an important role and be of the same order or higher than the charge–transfer interactions, as previously observed in Pt(II)-based molecular tweezers of a similar nature.[13a] In addition to these factors, the association constants are moderate and the solubility of the coordination complexes is low, and therefore the concentration of the inclusion complexes is expected to be very low under the experimental conditions. This effect is also observed in the emission spectra (Fig. S72, ESI†), in which the fluorescence quenching is almost negligible, and in the cyclic voltammograms (Fig. S73 and S74, ESI†), where the fullerene reduction potentials are not significantly shifted. Computational modelling using DFT methods was carried out to obtain further insight into the structure of the supramolecular adducts in solution (details in the ESI†). The geometries of inclusion complexes **C$_{60}$@Cu1a** and **C$_{60}$@Cu2a** were optimized, and the former is depicted in Fig. 3(c). The distances between the centroids of the corannulene fragments are 11.7 Å and 13.1 Å, respectively. The presence of the ethynyl spacer enlarges the cavity by *ca.* 1.4 Å. This translates into average corannulene-centroid–C_{60} distances of 3.4 Å for assembly **C$_{60}$@Cu1a** and

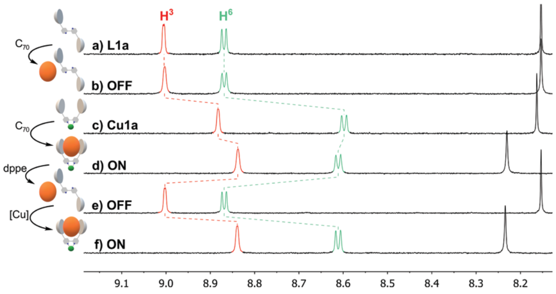

Fig. 2 Mode of operation of the **Cu1a/L1a** system and its behaviour towards C_{70} as monitored using ^{1}H-NMR in CD_2Cl_2 at 298 K.

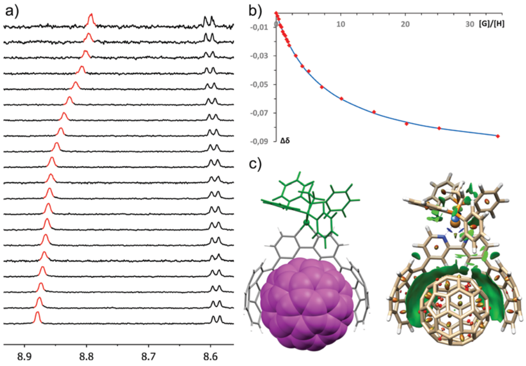

Fig. 3 (a) Selected region of the ^{1}H-NMR spectra for the supramolecular titration of **Cu1a** with C_{60} in CD_2Cl_2 at 298 K. (b) Plot of the changes in the chemical shift (Δδ) of H^3 against $[G]/[H]$, where G is C_{60} and H is **Cu1a**. The blue line corresponds to the nonlinear fitting of Δδ for proton H^3 to a 1 : 1 binding isotherm. (c) DFT-optimized geometry of assembly **C$_{60}$@Cu1a** and its corresponding NCI plot as gradient isosurface.

3.6 Å for assembly **C_{60}@Cu2a**, both of which are suitable for efficient attractive supramolecular interactions. This suggests that complex **Cu2a**, despite being rather rigid, still possesses sufficient flexibility to accommodate a fullerene molecule. This feature is also reflected in the marginal difference in their experimental K_a values, calculated electronic interaction energies (0.6 kcal mol^{-1}) and their similar NCI surfaces, which enclose a substantial portion of the outer fullerene surface (Fig. 3c and ESI†).

In summary, we have developed a straightforward synthesis of molecular tweezers based on bpy compounds bearing concave corannulene fragments whose fullerene recognition abilities can be modulated by a chemical effector through the *in situ* formation of tetrahedral Cu(I) complexes. We have demonstrated that the process is reversible and that the metal-mediated switching can be easily accomplished. The recognition is completely deactivated in the OFF state, whereas good binding affinities are observed in the ON state, being one order of magnitude greater for C_{70} *versus* C_{60}. Although the system is quite rigid, it still exhibits adaptability, as demonstrated by the binding affinities observed for the two molecular tweezers with different cavity sizes, establishing a subtle balance between entropy-penalizing mild flexibility and size complementarity.

We thank the Spanish Ministry of Science, Innovation and Universities (MCIU) for funding (project numbers PGC2018-096880-A-I00, MCIU/AEI/FEDER, UE, PGC2018-099470-B-I00, and MCIU/AEI/FEDER, UE). R. G.-R. acknowledges the Spanish MINECO/AEI and the European Union (ESF) for a Ramón y Cajal contract (RYC-2015-19035). H. B. acknowledges the Alfonso Martín Escudero Foundation for a postdoctoral fellowship.

Conflicts of interest

There are no conflicts to declare.

Notes and references

§ Provided that the byproduct build-up does not interfere with the chemical processes or the observation of this phenomenon. This is not the case after 5 cycles.

¶ Note that this feature is fundamental for fullerene recognition. To demonstrate the key role of corannulene in our ligand design, we prepared pyrene-based ligands (**L1b** and **L2b**) along with their Cu(I) complexes (**Cu1b** and **Cu1b**) and tested their fullerene recognition ability, which furnished negative results in all cases, evidencing that their planar structure is not suitable for molecular tweezers with this design (ESI†).

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