CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901206

A Double Plug–Socket System Capable of Molecular Keypad Locks through Controllable Photooxidation

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Abstract: Two robust divalent complexes have been successfully constructed by using complementary rigid spacers (anthracene vs. 1,4,5,8-naphthalenediimide (NDI)) and two pairs of [24]crown-8 ethers and secondary dialkylammonium functionalities as binding motifs. It was demonstrated that properly selected, rigid spacers are more efficient than flexible ones for achieving strong multivalent association. This is presumably due to the preorganization of the rigid spacers, the cooperation between charge-transfer interactions of rigid spacers, and the complexation of the binding motifs. Furthermore, the intermolecular photoinduced electron transfer (PET) between rigid spacers in these robust complexes could be switched on and off by modulating their complexation through acid–base reactions, which is reminiscent of a plug–socket system capable of electron transfer. In addition, the self-sensitized photooxidation of the divalent host with anthracene as a spacer can be completely inhibited after complexation with the divalent guests that contain NDI as spacers. This process could also be understood by invoking intermolecular PET and could be turned on and off through acid–base reactions. The photophysical and photochemical properties of these robust complexes have been interpreted as molecular keypad locks with alarm systems. Thus, a double plug–socket system and molecular keypad locks were successfully integrated inside robust multivalent systems and then the normal molecular devices were endowed with logic functions.

Keywords: logic gate · multivalency · photooxidation · self-assembly · supramolecular chemistry

Introduction

The bottom-up construction of molecular machines and devices[1] has attracted extensive attention in the last two decades due to the potential applications of these machines and devices as smart materials. A molecular plug–socket system is a sort of supramolecular species, which can be disassembled and reassembled by modulating the interactions that keep the components together.[2] The plug–socket systems have been demonstrated to carry out switching of electron- or energy-transfer processes[3] and could be useful for information processing at the molecular level. In the macroscopic world, logic devices are built into normal machines and devices to endow them with logic functions. Analogously, molecular plug–socket systems may also cooperate with molecular logic devices to perform more complex functions, which may even allow such a system to make a decision by itself.[4]

The development of molecular logic gates,[5] as an emerging research field, has inspired many scientists to try and solve the miniaturization problems faced by Si-based electronics. Since the first explicit correlation of Boolean logic with molecules synthesized by de Silva et al.,[6] numerous molecules capable of basic logic functions, including AND,[6,7] OR,[8] NAND,[9] INHIBIT,[10] NOR,[11] XOR,[12] and XNOR,[13] have been presented in the literature. Molecular combinatorial logic circuits, such as a digital adder,[14,15] subtractor,[15,16] comparator,[15e,17] and multiplexer,[18] have also been realized. More recently, a molecular keypad lock,[19] one of the most important achievements in this field, was successfully demonstrated and involves a system

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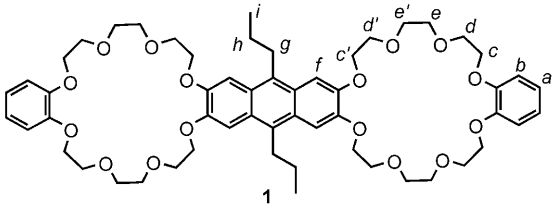
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901206.

in which the output signal is dependent on both the combination of inputs and their inputting sequence. It is worth emphasizing that it is the first nonlinear logic circuit to be described with single molecules. Besides the functional complexity, diverse logic functions can also be integrated inside single molecules through superposition[12a] or reconfiguration.[20] Although highly complex logic functions can be achieved with single molecules, a molecular computer is a more complicated device. Interconnection[5c,21] between different logic devices is required to create more complex logic circuits, which still remains as a challenge in this field. As learned from natural systems, self-assembly[22] and self-sorting[23] may work as a glue to interconnect different molecular logic gates and thus achieve higher-level logic functions. From this point of view, logic gates based on molecular assemblies[24] are even desirable for the construction of a molecular computer. In addition, the advantage of the molecular logic gate relies on the size of a single molecule. Therefore, the integrity of self-assembled logic devices has to be ensured for the execution of logic functions at the single-molecule/assembly level. This problem may be resolved by harnessing multivalent effects.

Multivalency[25] is an important concept in supramolecular chemistry. It not only governs numerous biological interactions in nature,[25a] but also provides a self-assembly approach for the construction of robust nanostructures and molecular machines.[26] In artificial systems, the multivalent effect is often improved by using flexible spacers and more valencies (binding motifs), however, this seems to lack efficiency. A strong multivalent effect could also be effectively achieved by using a highly complementary multivalent host–guest system; rigid spacers can be used to achieve the desired arrangement of the host and guest.[27] Design of such a complementary host–guest system, however, requires very careful selection of complementary spacers and binding motifs, even to nano- or picometer accuracy,[25b] otherwise it may lead to even weaker binding affinities than the corresponding multivalent systems with flexible spacers.

Herein, we report the first molecular keypad locks based on robust self-assembled systems; [24]crown-8 ethers and secondary dialkylammonium groups are selected as the binding motifs and anthracene (in divalent host **1**) and 1,4,5,8-naphthalenediimide (NDI) (in divalent guest [**2**-H_2][PF_6]$_2$) as rigid spacers for the construction of the robust multivalent systems. The resulting binding affinity in these systems was proven to be much stronger than that between **1** and divalent guest [**3**-H_2][PF_6]$_2$ with a flexible spacer, presumably derived from improved multivalent effect and cooperation. Furthermore, the divalent complex [**1**·**2**-H_2][PF_6]$_2$ was demonstrated to be a double plug–socket system capable of intermolecular photoinduced electron transfer (PET) by the control of their disassembly/reassembly through an acid–base reaction. This complex was, therefore, found to work as a switchable "molecular shield" to protect the anthracene moiety in **1** from self-sensitized photooxidation through intermolecular PET from an excited anthracene of **1** to NDI of [**2**-H_2][PF_6]$_2$. As one step further, two molecular keypad locks with alarm systems are superposed with the double plug–socket system according to the controllable supramolecular photochemical and photophysical properties of [**1**·**2**-H_2][PF_6]$_2$.



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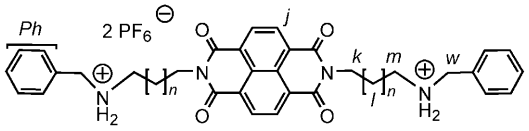
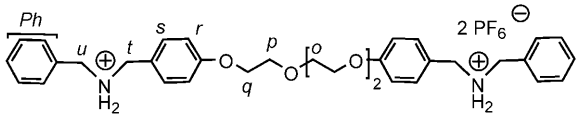
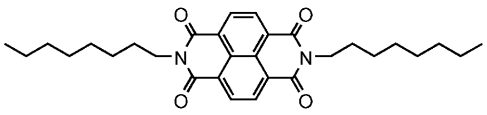


n=0, [**2a**-H_2][PF_6]$_2$
n=1, [**2b**-H_2][PF_6]$_2$



[**3**-H_2][PF_6]$_2$



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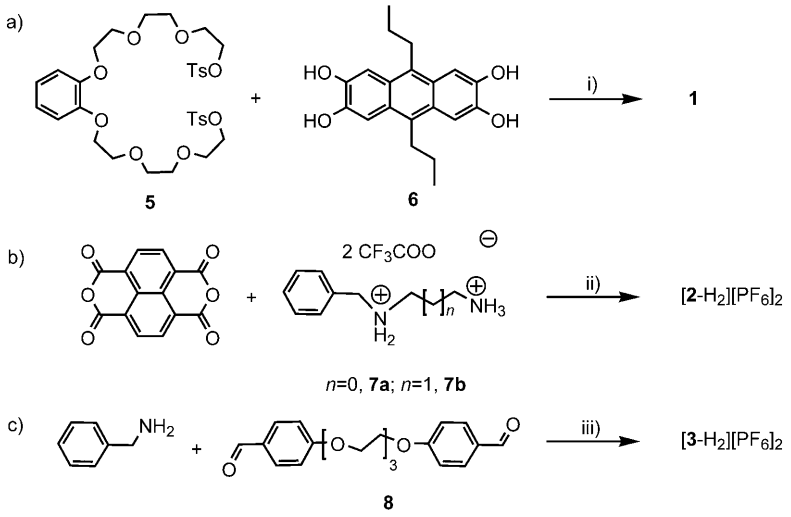
Results and Discussion

Synthesis: The anthracene-bridged divalent host **1** was synthesized in a convergent manner from two intermediate compounds **5** and **6** in a reasonable yield (20%) (Scheme 1a). The divalent guests [**2a**-H_2][PF_6]$_2$ and [**2b**-H_2]-[PF_6]$_2$ (Scheme 1b) with NDI as the rigid spacer and [**3**-H_2]-[PF_6]$_2$ (Scheme 1c) with triethylene glycol as a flexible spacer were achieved from amidation and Schiff base reactions, respectively, followed by protonation and counterion exchange.

Multivalent interactions: Multivalent association between the divalent host **1** and the divalent guest [**3**-H_2][PF_6]$_2$, which has a flexible spacer, was established by NMR spectroscopy and electrospray ionization mass spectrometry (ESIMS) experiments. As shown in Figure 1, the downfield shifts of H_t and H_u indicate the pseudorotaxane structure complexation between the [24]crown-8 ether and the secondary dialkylammonium group. The striking upfield shifts of H_r ($\delta = -0.61$ ppm) and H_s ($\delta = -0.35$ ppm) are likely to be due to shielding by the aromatic ring current of anthracene in **1**, which strongly suggests that a 1:1 adduct [**1**·**3**-H_2][PF_6]$_2$ with H_r and H_s on top of anthracene is formed in solution. Interestingly, H_q is shifted downfield, presumably resulting from the π–π stacking and hydrogen-bonding interactions



Scheme 1. Synthetic procedures to divalent host **1** (a), and divalent guests [**2**-H_2][PF_6]$_2$ (b) and [**3**-H_2][PF_6]$_2$ (c). i) Cs_2CO_3, dry MeCN, reflux, 5 d; ii) 1) Et_3N, *i*PrOH, reflux, 3 d; 2) concentrated HCl, MeOH; 3. NH_4PF_6, acetone; iii) 1) CH_3OH, reflux, 24 h; 2) $NaBH_4$, reflux, 24 h; 3) concd HCl, MeOH; 4. NH_4PF_6, acetone.

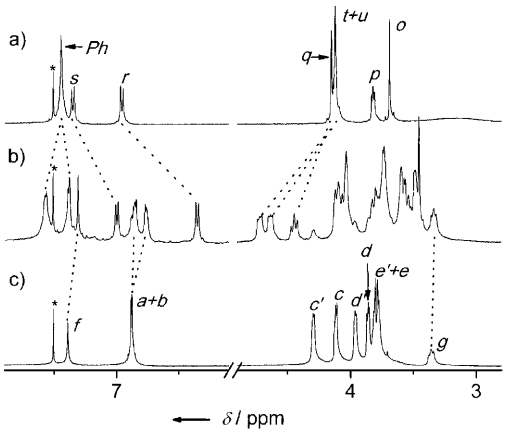


Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 5 mM, 298 K) of [**3**-H_2][PF_6]$_2$ (a), 1:1 adduct [**1**·**3**-H_2][PF_6]$_2$ (b), and **1** (c). * = residual solvent.

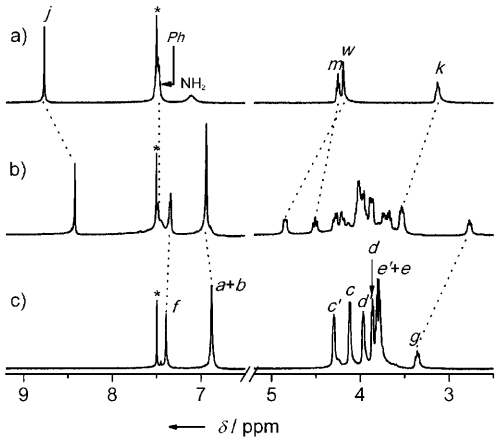


Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 5 mM, 298 K) of [**2b**-H_2][PF_6]$_2$ (a), 1:1 adduct [**1**·**2b**-H_2][PF_6]$_2$ (b), and **1** (c). * = residual solvent.

between **1** and [**3**-H_2][PF_6]$_2$, which directs the flexible triethylene glycol spacer to the deshielding field of anthracene. The 1:1 binding stoichiometry between **1** and [**3**-H_2][PF_6]$_2$ was further confirmed by ESIMS experiments (Figures S10 and S11 in the Supporting Information).

As noted above, the design of well-complementary multivalent systems with rigid spacers requires nano- or picometer accuracy.[25b] To test the complementarity between the anthracene of the host and the NDI of the guest, NMR spectroscopy and ESIMS experiments were performed on an equimolar mixture of the two substrates. The strong multivalent interactions between **1** and [**2b**-H_2][PF_6]$_2$ are clearly indicated by the obvious and complete downfield shifts of H_m (δ = 0.26 ppm) and H_w (δ = 0.65 ppm) relative to free [**2b**-H_2][PF_6]$_2$ (Figure 2). Meanwhile, the large upfield shifts of H_j (δ = −0.35 ppm) and H_g (δ = −0.59 ppm) should result from the mutual shielding effects between the anthracene of the host and the NDI of the guest. These observations suggest that the 1:1 complex [**1**·**2b**-H_2][PF_6]$_2$ in which anthracene and NDI are located directly over each other dominates in the equimolar mixture of **1** and [**2b**-H_2][PF_6]$_2$, which is also supported by the Job's plot (Figure S12 in the Supporting Information). The strong binding affinity and 1:1 stoichiometry was further confirmed by an ESI mass spectrum in which only one intense peak at *m*/*z* 783 attributed to [**1**·**2b**-H_2]$^{2+}$ was observed (Figure 3). Analogously, the exclusive formation of [**1**·**2a**-H_2][PF_6]$_2$ from **1** and [**2a**-H_2][PF_6]$_2$ has also been confirmed from the ^{1}H NMR and ^{1}H–^{1}H COSY spectra and the ESIMS experiments (Figures S14–S16 in the Supporting Information).

To obtain the information on the superiority of a rigid spacer over a flexible one in multivalent association, ^{1}H NMR spectroscopy experiments on 1:1:1 mixture of **1**, [**2**-H_2][PF_6]$_2$, and [**3**-H_2][PF_6]$_2$ were performed (Figure S17 in the Supporting Information). According to the integral values of H_j(uc), H_j(c), and H_r(c) in **1**, [**2**-H_2][PF_6]$_2$, and [**3**-H_2][PF_6]$_2$, we estimated that the association constant[28] between **1** and [**2**-H_2][PF_6]$_2$ is two orders of magnitude higher than that between **1** and [**3**-H_2][PF_6]$_2$. That is to say, compound **1** binds more strongly to [**2**-H_2][PF_6]$_2$ than to [**3**-H_2]-[PF_6]$_2$ and the carefully selected rigid spacer (NDI vs. anthracene) is more suitable for forming a multivalent complex. In the present case, the rigid spacers in **1** and [**2**-H_2]-

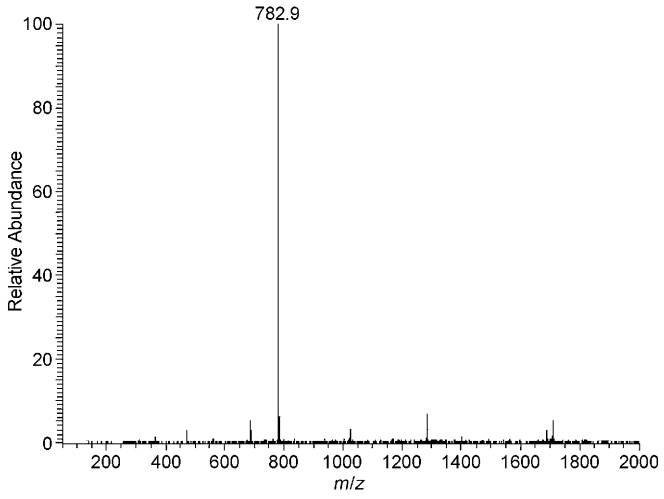


Figure 3. ESIMS (low resolution) spectrum of the equimolar mixture of **1** and [**2b**-H_2][PF_6]$_2$ (0.1 mmol) in $CDCl_3$/CD_3CN (1:1). The major peak at *m*/*z* 783 is assigned to the dication [**1·2b**-H_2]$^{2+}$.

[PF_6]$_2$ preorganize the binding motif, which leads to the two pairs of [24]crown-8 ether and the secondary ammonium groups being in the perfect position for multivalent association. This thus improves the efficiency of multivalency to achieve a strong association between the host and the guest by use of a minimum binding motif.

To further understand the roles of rigid spacers in the enhancement of the binding affinity, we performed absorption experiments on **1**, [**2b**-H_2][PF_6]$_2$, and [**1·2b**-H_2][PF_6]$_2$. A new absorption band centered at 620 nm is observed in the spectrum of [**1·2b**-H_2][PF_6]$_2$ relative to the free host and guest (Figure 4), which indicates the presence of charge transfer (CT) upon complexation of **1** with [**2b**-H_2][PF_6]$_2$. This is also in agreement with the color change from light yellow of both **1** and [**2**-H_2][PF_6]$_2$ to dark green of [**1·2**-H_2][PF_6]$_2$ at high concentration (5 mM). No obvious interaction was observed between **1** and neutral **2**, or between **1** and **4** (Figure S19 in the Supporting Information). It is likely that the complementary rigid spacers in **1** and [**2b**-H_2][PF_6]$_2$ enhance

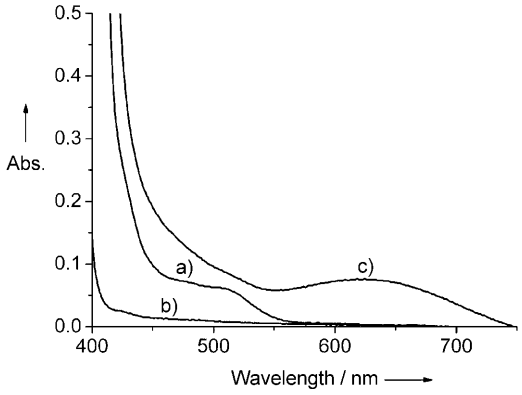
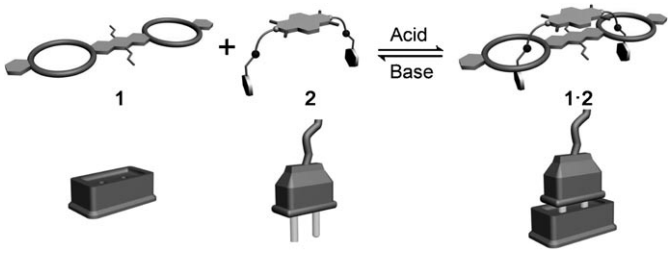


Figure 4. Absorption spectra of **1** (a), [**2b**-H_2][PF_6]$_2$ (b), and [**1·2b**-H_2]-[PF_6]$_2$ (c) ($CDCl_3$/CD_3CN = 1:1, 1.5 mM).

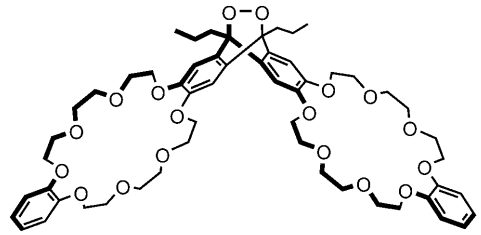
the multivalent association between the two binding motifs and, in return, the strong multivalent binding gathers anthracene and NDI close enough for CT interactions to form, which further contributes to the enhanced binding affinity between **1** and [**2b**-H_2][PF_6]$_2$. In other words, the CT interactions between the rigid spacers and the multivalent association between the binding motifs cooperate to contribute to the enhanced binding affinity between **1** and [**2**-H_2][PF_6]$_2$.

In addition, the disassembly/reassembly of [**1·2**-H_2][PF_6]$_2$ could be achieved by well-established acid/base chemistry (Figures S20 and S21 in the Supporting Information).[26f] This is reminiscent of a double plug–socket system, especially when considering the intermolecular PET process from electron-rich anthracene[29] to electron-poor NDI[30] during excitation of [**1·2**-H_2][PF_6]$_2$ (see below). The schematic representation of the double plug–socket species is illustrated in Scheme 2.



Scheme 2. The schematic representation of the double plug–socket species.

Controllable photooxidation: As is well known, there are two types[31] of photosensitized oxidation. Both reactions involve the absorption of light by a sensitizer to produce an excited sensitizer. Type I is a reaction in which the radical or radical ions evolved from an excited sensitizer react with the ground-state oxygen ($^3O_2$) to give photooxygenated compounds. For type II, the excited oxygen ($^1O_2$) is first produced by the triplet state of an excited sensitizer and then adds to substrates to produce oxygenated products. In the absence of other sensitizers, unsubstituted anthracene is relatively more stable to visible light in solution than the larger acenes, which may undergo self-sensitized photooxidation.[32] Surprisingly, without any other sensitizer, compound **1** can also be photooxidized in solution to produce an endoperoxide (**1**·O_2; Scheme 3) in which O_2 is added at the 9,10-positions of anthracene, which is clearly validated by the disappearance or the shift in resonance of the aromatic-ring-current-shielded protons $H_{c'}$, $H_{d'}$, H_f, and H_g of **1** after irradiation by visible light (Figure 5a, b). This observation is also supported by time-dependent ^{1}H NMR and UV-visible spectroscopies, and ESI mass spectrometry (Figures S18–S22 in the Supporting Information). Presumably, the four electron-donating ether substituents in **1** enhance the reactivity of anthracene towards $^1O_2$[33] and the propyl groups in the 9,10-positions of anthracene cause steric hindrance for photodimerization and favor photooxidation.[34] Consequently, the



$1{\cdot}O_2$

Scheme 3. Chemical structure of photooxygenated **1** (**1**·O_2).

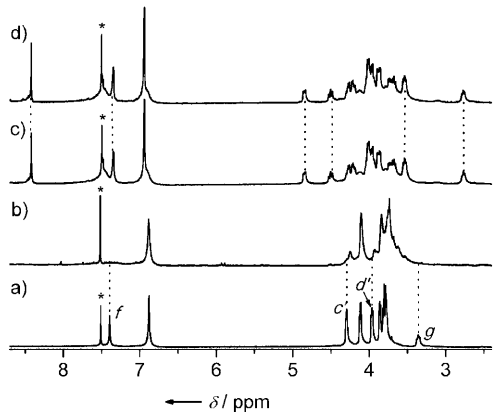


Figure 5. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1:1, 5 mM, 298 K) of **1** before (a) and after (b) irradiation by visible light, and [**1·2b**-H_2][PF_6]$_2$ before (c) and after (d) irradiation by visible light. * = residual solvent.

photooxidation of **1** is probably due to a self-sensitized process.

Surprisingly, after formation of the divalent complex [**1·2**-H_2][PF_6]$_2$, **1** can be protected from photooxidation. The ^{1}H NMR spectrum of [**1·2b**-H_2][PF_6]$_2$ showed no obvious changes, even after four months of solar irradiation (Figure 5c, d). That is, compound [**2**-H_2][PF_6]$_2$ can work as a molecular shield to protect **1** from photooxidation. The phenomenon could be understood by invoking an intermolecular PET process from excited anthracene to NDI and by the high binding affinity between **1** and [**2**-H_2][PF_6]$_2$. During the solar irradiation, some parts of the excited anthracenes are relaxed through the PET process and not much energy can be used for the conversion of $^3O_2$ to $^1O_2$. Thus, $^1O_2$ for photooxidation is not available. In addition, considering the high binding affinities between **1** and [**2**-H_2][PF_6]$_2$, the concentration of the free host and guest are very low in solution and cannot be seen in the ^{1}H NMR spectrum (Figure 5 and Figure S14 in the Supporting Information). As a result, the divalent complexes [**1·2**-H_2][PF_6]$_2$ are the only predominant species in this solution. The photooxidation, however, has to occur between free **1** and $^1O_2$, but both of them are rare in this solution.[35] Moreover, the photooxidation of **1** will obviously change its conformation from a relatively "planar" structure to a "dihedral" structure, and thus decreases the distance between the two crown ether motifs of **1**. The photooxygenated complex of **1** (**1**·O_2)[36] is unsuitable to form a divalent complex with [**2**-H_2][PF_6]$_2$. It can also be ruled out that a concerted process, which involves the simultaneous formation of **1**·O_2 and the disassembly of [**2**-H_2][PF_6]$_2$, exists because of the high binding affinity and the slow kinetics between **1** and [**2**-H_2][PF_6]$_2$.

As seen in Figure 6, the fluorescence of [**1·2b**-H_2][PF_6]$_2$ shows no obvious change after irradiation by visible light (Figure 6, line b). Upon the addition of an excess of base to

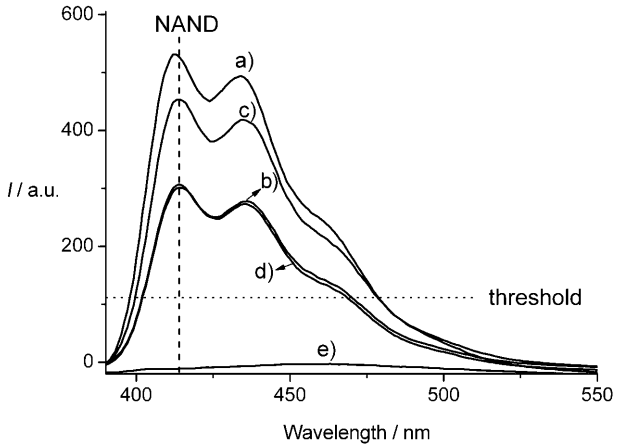


Figure 6. Emission spectra ($CDCl_3/CD_3CN$ = 1:1, 0.01 mM, excited at λ = 375 nm) of **1** (a), [**1·2b**-H_2][PF_6]$_2$ with and without irradiation of visible light (b), [**1·2b**-H_2][PF_6]$_2$ after the addition of 5 equiv of $(Bu)_3N$ (c) or $(Bu)_3N$ and CF_3COOH (d), and [**1·2b**-H_2][PF_6]$_2$ after the addition of 5 equiv of $(Bu)_3N$ and irradiation by visible light (e). [**1·2b**-H_2][PF_6]$_2$ can work as a NAND logic gate with the addition of a base and then irradiation with visible light as sequential inputs.

a solution of [**1·2**-H_2][PF_6]$_2$, compound **1** is released from the shield of [**2**-H_2][PF_6]$_2$ and can then be photooxidized. The PET process is partly switched off by the addition of acid and the emission intensity was found to increase (Figure 6, line c), although it is still lower than that of **1** probably due to the existence of long-range PET and absorption competition by neutral **2b** (Figure S27 in the Supporting Information). With the presence of excess base, neutral **2b** cannot protect **1**. Uncomplexed **1** was therefore photooxidized to the nonfluorescent state (**1**·O_2; Figure 6, line e). When the nonfluorescent solution was heated, the O_2 from **1**·O_2 was released and the florescence was recovered. Without irradiation, the assembly and disassembly of [**1·2**-H_2][PF_6]$_2$ can be reversibly controlled and the emission intensity recovered to the original state (Figure 6, line d) by the addition of base and then acid for at least five repeating cycles,.

Molecular keypad lock: With base and visible light as inputs and the fluorescent intensity at 415 nm as an output, a NAND logic gate can be constructed from the solution of [**1·2b**-H_2][PF_6]$_2$. The NAND logic function is highly reliant on the sequence of the two inputs. With no input (Figure 6, line b), inputting either one of the two inputs (Figure 6, lines b and c), or first inputting visible light and then base (line c), the output signal is on (1). Only the sequential

input of first base and then visible light (Figure 6, line e) can switch off the fluorescence of [**1·2b**-H_2][PF_6]$_2$ (0).

This input-sequence-specific NAND logic gate can be further interpreted as a two-digit molecular keypad lock with base (B) and visible light (L) as inputs (Figure 7a, b). Only the two-digit sequential input BL can switch off the fluorescence of [**1·2b**-H_2][PF_6]$_2$ and this is used as the password. Interestingly, the inputting of the reverse sequence (LB) will increase the emission intensity at 415 nm by 50%, which makes it a perfect alarm system to warn or scare away the "thief" who puts in the wrong sequence, but it also makes the brave thief closer to the password.

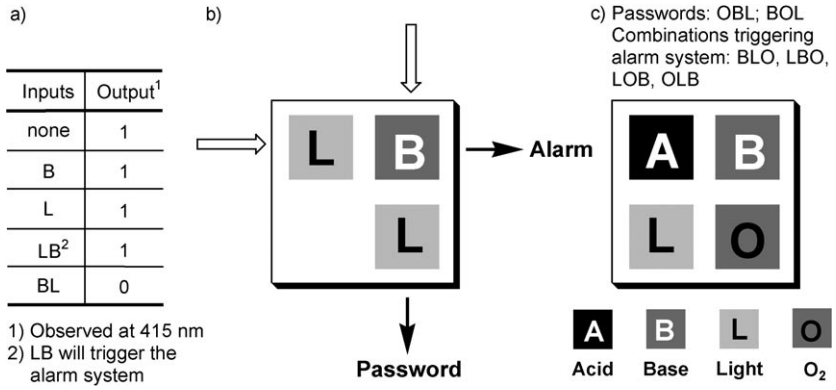


Figure 7. The truth table (a) of a two-digit molecular keypad lock with alarm system (b), and an improved molecular keypad lock with four possible inputs and two three-digit passwords (c).

Considering the oxidation process, O_2 is indispensable and can be removed by normal degassing processes. Therefore, O_2 (O) can also be considered as another input. With acid (A) as an interfering input, the combination amongst the four inputs (A, B, L, and O) is complex enough to avoid deciphering the password. Two three-digit combinations (OBL and BOL) are the passwords for the improved molecular keypad lock (Figure 7c), which may allow two independent people to have their own keys. The different sequential organization of the same inputs, BLO, LBO, LOB, and OLB, will trigger the alarm system and make the keypad lock even safer. As discussed above, the recycling of this keypad lock system could be achieved by heating and the addition of acid. Noticeably, the two molecular keypad locks presented above rely solely on the equilibrium states, not on the kinetic behavior of this system, which may make them unrestricted by a long operation time.

Conclusion

We have successfully demonstrated a double plug–socket system capable of electron transfer based on robust multivalent complexes with complementary rigid spacers, which were proven to be superior to a flexible spacer. The enhanced binding affinity results, not only from the improved multivalent effects through the preorganization of rigid spacers, but also from the cooperation between two pairs of binding motifs and a pair of electronically complementary spacers. The intermolecular PET process from one rigid spacer (anthracene) to the other (NDI) during the excitation of the complexes could be switched on and off by controlling the disassembly and reassembly with an acid–base reaction, which is reminiscent of a double plug–socket system. Furthermore, the self-sensitized photooxidation of an uncomplexed host with anthracene as a spacer could be shut down upon complexation with divalent guests with NDI as a spacer. Therefore, the photophysical and photochemical properties of the complexes could be finely modulated. By using these features, with monitoring fluorescence change as output, the robust multivalent complexes have been interpreted as molecular keypad locks with additional alarm systems, which are only dependent on the equilibrium states and not on the kinetic behavior of this system.[4] Finally, the double plug–socket system and molecular keypad locks are integrated inside the robust multivalent complexes. Thus, normal molecular devices are made more intelligent by the cooperation with molecular logic gates.

Experimental Section

General: All reagents, unless otherwise indicated, were obtained from commercial sources. Compound **4**,[37] **5**,[38] and **7**[39] were synthesized according to literature procedures. Analytical-grade MeCN was dried over P_2O_5 at room temperature for 2 d and then distilled to give the anhydrous solvent for reaction. Commercially available chromatography-grade MeCN was used for UV and fluorescence measurements. Anhydrous $CHCl_3$ was obtained by distillation from CaH_2. Melting points were determined on a XT-4 melting-point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VS400 NMR spectrometer. All chemical shifts are reported in ppm with residual solvents as the internal standards; the coupling constants (J) are in Hertz. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. Low-resolution ESIMS and high-resolution ESIMS were obtained on a Thermofinnigan LCQ Advantage ESI mass spectrometer and a Ionspec ESIHRMS (7.0 T) mass spectrometer, respectively. The electrospray ionization Fourier-transform ion cyclotron resonance (ESI-FT-ICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer (7.0 T). Absorption spectra were recorded with a Shinadazu UV-2401PC instrument. Fluorescence spectra were measured in a conventional quartz cell (10×10×45 mm) at 25°C on a JASCO FP-750 spectrometer with excitation and emission slits 5 nm in width.

Anthracene bis-crown ether 1: A suspension of Cs_2CO_3 (6.60 g, 20 mmol) in anhydrous MeCN (150 mL) under an N_2 atmosphere was stirred vigorously and heated to reflux. A solution of **5** (2.70 g, 4 mmol) and **6** (0.65 g, 2 mmol) in anhydrous MeCN (200 mL) was added dropwise to the suspension over 48 h. The reaction mixture was stirred under reflux for an additional 3 d. After cooling to room temperature, the reaction mixture was removed by filtration and the residue was washed with

CH_2Cl_2 (150 mL). The filtrate was concentrated under reduced pressure to give a dark tar, which was partitioned between CH_2Cl_2 (150 mL) and H_2O (150 mL). The aqueous layer was washed with CH_2Cl_2 (2×50 mL). The organic layer was combined, dried (anhydrous Na_2SO_4), and concentrated under reduced pressure to afford the crude product, which was subjected to column chromatography (silica gel; eluent: 100:1 CH_2Cl_2/CH_3OH). The obtained solid was recrystallized from $CHCl_3$/isopropyl alcohol (2:1) and then washed with methanol to give **1** as a yellowish solid (400 mg, 20%). M.p. 182–184°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.10 (t, J=7.2 Hz, 6H), 1.74–1.83 (m, 4H), 3.33 (t, J=7.2 Hz, 4H), 3.84–3.95 (m, 24H), 4.03–4.05 (m, 8H), 4.14–4.16 (m, 8H), 4.30–4.32 (m, 8H), 6.85–6.86 (m, 8H), 7.36 ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.1, 23.9, 30.9, 69.3, 69.6, 70.0, 70.2, 71.5, 71.6, 104.7, 114.2, 121.6, 125.8, 129.6, 148.5, 149.1 ppm; HRMS (ESI): m/z: calcd for $C_{55}H_{74}O_{16}Na$: 1025.4869; found: 1025.4862.

Divalent guests [2a-H_2][PF_6]$_2$ and [2b-H_2][PF_6]$_2$: Compounds **7a** or **7b** (4.5 mmol) and Et_3N (18 mL, 26 mmol) were added to a mechanically stirred suspension of 1,8,4,5-naphtalene dianhydride (536 mg, 2 mmol) in *i*PrOH (70 mL). The resulting mixture was heated at reflux for 3 d. After cooling to room temperature, a yellow solid formed that was removed by filtration and washed with *i*PrOH. The yellow solid was dissolved in MeOH (40 mL) and concentrated HCl was added to adjust to pH 2. The reaction mixture was stirred at room temperature for another 4 h and the solvent was evaporated. After the residue was washed with CH_2Cl_2, a yellow solid was obtained. The yellow solid was suspended in acetone (60 mL) and a saturated solution of NH_4PF_6 (3.26 g, 20 mmol) was added. The reaction mixture was stirred overnight at room temperature and evaporated under reduced pressure. The residue was suspended in water (100 mL) and stirred at room temperature for 5 h. The mixture was then filtered and the solid washed with water. The filter cake was recrystallized from CH_3Cl/MeCN and dried to afford the product as a yellow solid.

[2a-H_2][PF_6]$_2$: Yield: 230 mg, 14%; M.p.>210°C (decomposition); ^{1}H NMR (400 MHz, CD_3CN): δ=3.50 (4H), 4.31 (s, 4H), 4.51 (4H), 7.42–7.53 (m, 10H), 8.80 ppm (s, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ=37.3, 46.8, 52.1, 126.9, 127.0, 129.4, 130.2, 130.5, 131.3, 142.5, 164.0 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{30}F_6N_4O_6P$: 679.19034; found: 679.19035.

[2b-H_2][PF_6]$_2$: Yield: 800 mg, 47%; M.p.> 236°C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.10–2.20 (m, 4H), 3.13 (t, J=6.4 Hz, 4H), 4.20 (s, 4H), 4.22 (t, J=6.4 Hz, 4H), 7.44–7.54 (m, 10H), 8.73 ppm (s, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ=25.2, 38.0, 46.2, 52.7, 127.6, 127.7, 130.1, 130.8, 131.0, 131.4, 131.8, 164.7 ppm; HRMS (ESI): m/z: calcd for $C_{34}H_{34}F_6N_4O_6P$: 707.2216; found: 707.2210.

Divalent guest [3-H_2][PF_6]$_2$: A solution of **8** (3.58 g, 10 mmol) and benzylamine (2.2 mL, 20 mmol) in MeOH (40 mL) was heated under reflux for 24 h. After the reaction mixture was cooled to room temperature, $NaBH_4$ (2.28 g, 60 mmol) was added in small portions before the reaction mixture was heated under reflux for a further 24 h. The solvent was evaporated under reduced pressure and the residue was partitioned between CH_2Cl_2 (100 mL) and water (100 mL). The aqueous layer was washed with CH_2Cl_2 (2×50 mL). The organic phases were combined and dried over Na_2SO_4. Filtration, followed by evaporation of the solvent resulted in a yellow oil. The yellow oil was dissolved in MeOH (20 mL) and concentrated HCl was added to adjust to pH 2. The reaction mixture was stirred at room temperature for a further 4 h and the solvent was evaporated. After the residue was washed with CH_2Cl_2, a white solid was obtained. The white solid was dissolved in acetone (30 mL) and a saturated solution of NH_4PF_6 was added until the solution become clear. The reaction mixture was stirred for another 3 h and the solvent was evaporated under reduced pressure. The residue was suspended in water (50 mL) and stirred at room temperature for 5 h. The mixture was filtered, the residue washed with water and dried in air to afford the product [3-H_2][PF_6]$_2$ as a white solid (3.70 g, 44%). M.p. 90–92°C; ^{1}H NMR (400 MHz, CD_3CN): δ=3.66 (s, 4H), 3.80 (t, J=4.8 Hz, 4H), 4.12–3.21 (m, 12H), 6.97 (d, J=8.8 Hz, 4H), 7.41 (d, J=8.4 Hz, 4H), 7.46–7.50 ppm (m, 10H). ^{13}C NMR (100 MHz, CD_3CN): δ=51.2, 51.4, 67.8, 69.4, 70.6, 115.1, 123.0, 129.3, 129.8, 130.3, 131.1, 132.0, 160.0 ppm; ESIMS: m/z: 541 [$M-2PF_6^- - H^+$]$^+$; 687 [$M-PF_6^-$]$^+$; 1519 [$2M-PF_6^-$]$^+$. HRMS(ESI): m/z: calcd for $C_{34}H_{42}N_2O_4$: 541.3061; found: 541.3061.

Acknowledgements

This work was supported by the 973 Program (2006CB932900), TNSF (07QTPTJC29700), NNSFC (Nos. 20721062 and 20772063), and the Program for New Century Excellent Talents in University (NCET-05–0222). We thank Prof. Dr. Christoph A. Schalley for help with the ESIFTICR experiments.

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Received: May 7, 2009
Published online: August 5, 2009

