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Sequential and combinational logic realized with asymmetric porphyrin covalently connected to mesoporous silica films

Peng Li [a,b], Bin Li [a,*], Liming Zhang [a,*], Jie Gao [a], Haifeng Zhao [a]

[a] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China
[b] Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

Here, an asymmetric porphyrin derivative of 5-(4-aminophenyl)-10, 15, 20-triphenyl-porphyrin (H_2ATPP) has been successfully covalently connected to photo-permeable mesoporous silica thin films as a unit to mimic logic function. This hybrid mesoporous structure is not only advantageous to the interaction between inputs and response materials, but also to separation of the response materials and inputs without information lost. Then several molecular logics with the function of memory, based on its characteristic of being sensitive to acid and base, are achieved. With different initial states, it could be handily described as feedback loop and RS-latch for sequential logic.

1. Introduction

In conventional digital circuits and systems, an integrated logic circuit could be categorized into two units, the combinational circuit for information processing and the sequential circuit for committing the consequence processed by the former unit to memory [1–5]. In 1993, the universality of molecular logic was realized by de Silva through a bistable molecular system, and its implementation can be carried out with non-electrical signal [6]. Over the past two decades, a series of similar molecular logics have been successfully simulated, including AND, OR, XOR, NOR. Some other complicated gates have also been proposed by combining various basic ones with others, such as adders-substractors [7–9], encoders–decoders [10,11], and multiplexers–demultiplexers [12]. For these samples, the current state couldn't be stored and thus has no consequence for the next state. Since then, another unit with memory as its major responsibility has been proposed. This feature connects the outputs of a logic gate back to one or more of its inputs, which could be regarded as a feedback loop, as firstly described by Raymo et al. [13]. Molecular logic unit with memory as its major function has been drawn much attention, lots of jobs have been carried out to achieve this amazing function [14–19]. In 2010, a Os(II) polypyridyl complex was covalently bonded to solid substrate to achieve RS-latch and other combinational logics by van der Boom group [20]. Since the response complex has been immobilized to solid substrates, it could not be wash away with the chemical inputs and its states would be retain even after the film was deviated from the chemical inputs [14,18,20]. On account of being immobilized on solid substrate, each oxidation state of the complex could be integrally stored and recycled without information loss [18,20].

On the other hand, porphyrin owns the nature of responding to both base and acid [7], accompanied with spectroscopic property variations, suggesting that porphyrin could be used to achieve various logic operations. For example, Langford et al. [7] has reported the operation of substractor. It is believed by us that if porphyrin can be covalently bonded to a series of mesoporous silica thin films, then each state of porphyrin should be stably stored even after it is deviated from the acid or base [18,20]. The mesoporous silica thin films also favor the efficient interaction between the inputs and the response materials by providing a large surface area [23], and the excess chemical input acid or base will be easily removed by washing with the corresponding solvents. Noteworthy, the covalently immobilized chromophore in the protonated or unprotonated form will be unaffected by the washing. This all suggests a promising potential of mesoporous silica thin films as substrates.

Enlightened by above research results, in this Letter, we intend to covalently bind controlled quantity of asymmetric porphyrin derivative to a photo-permeable mesoporous silica thin film owing highly ordered mesoporous structure [21]. It is expected that an uncomplicated memory device and a RS-latch can be constructed.

2. Experiment

Concentrated HCl, tetrahydrofuran (THF), tetraethyl orthosilicate (TEOS), and ethanol were commercially obtained from Beijing Chemical Company. The water used in our present work was deionized. The solvent of THF was purified by distillation in a vacuum. The silane coupling agent of (3-isocyanatopropyl)triethoxysilane (ICPTES) was purchased from Tokyo Chemical Industry (TCI)

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* Corresponding authors. Fax: +86431 86176935.
E-mail addresses: lib020@yahoo.cn (B. Li), zhanglm770@163.com (L. Zhang).

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and covalently linked with porphyrin by a urea bond, forming the modified organic silica (ATPP–Si) [21]. Without further purification, it was immediately used for preparing the mesoporous silica thin films [22]. Consulting a series of literature procedures [23,25,26], a two-step synthetic process was employed to fabricate the organic–inorganic hybrid mesoporous thin film bearing porphyrin, using the sol–gel procedure with cetyltrimethyl ammonium bromide (CTAB) as surfactant. Spin-coating was adopted to obtain thin films on glass slides or quartzes.

The porphyrin derivative of 5-(4-aminophenyl)-15, 20, 25-triphenylporphyrin (ATPP) was prepared and purified according to a literature protocol [24]. ^{1}H NMR (CD_3Cl): δ 8.94 (d, 2H), 8.83 (s, 6H), 8.22 (d, 6H), 8.00 (d, 2H), 7.76 (m, 9H), 7.04 (d, 2H), 4.02 (s, 2H), −2.73 (s, 2H); IR (cm^{-1}, KBr): NH stretch (3442, 3380 and 3317 cm^{-1}); NH stretch (1616 cm^{-1}). The HPLC data of the compound, which identify the the homogeneity and purity, is shown in Supporting information.

Excess ICPTES (0.0080 mL) was added to a solution of ATPP (0.0010 g) in anhydrous THF (4 mL) under stirring. After stirring for about 30 min, the mixture was heated to 70 °C and kept for 24 h under nitrogen atmosphere. Excessive THF was removed by rotary evaporation under reduced pressure. Then 20 mL of cold dry hexane was added into the residue to form precipitate. The precipitate was filtered and washed with several portions of cold dry hexane and dried in vacuum. IR (cm^{-1}, KBr): NH stretch (3401 cm^{-1}), NH–CO–NH stretch (1695, 1649, 1595 and 1537 cm^{-1}).

2.1. Preparation of the hybrid thin films

First, ATPP (0.0001 g) was used to prepare ATPP–Si followed by evaporation of the THF. Without further purification, ATPP–Si was reacted with TEOS (1.0 mL), ethanol (1.0 mL), H_2O (0.312 mL), and HCl (0.012 mL, 0.07 mol/L) under gently and simultaneously stirring. The original mole ratio of the mixture is TEOS/EtOH/H_2O/HCl/ATPP–Si = 1:3.8:1:5 × 10^{-5}:3.54 × 10^{-5}. The resulting reaction mixture was refluxed at 60 °C for 90 min. After cooling to room temperature, 0.148 mL of water and 0.5 mL of HCl (0.07 mol/l) were added to adjust the concentration of HCl ([HCl]) to 7.34 × 10^{-3} mol/L. After stirring for 15 min at 25 °C, the mixture was aged at 50 °C for another 15 min and diluted with ethanol. Finally, the surfactant of CTAB was added to turn the mole ratio of the mixture into 1 TEOS: 22 EtOH: 5 H_2O: 0.004 HCl: 0.096 CTAB: 3.54 × 10^{-5} ATPP–Si.

Glass slides and quartzes were taken as substrates and cleaned according to a literature method [1,25]. The hybrid thin films were then deposited onto those substrates by spin-coating at 3000 rpm. They were stored at room temperature for 6 days to evaporate the solvent, and further aged in an oven at 100 °C for 24 h [26]. The surfactant CTAB and unreacted porphyrin were extracted firstly by 50 mL acetone for 7 h, and followed by 50 mL HCl–EtOH (1 mol/L) for 12 h both in Soxhlet extractor [22,25]. Based on analyzing the absorption spectrum of porphyrin extracted by acetone, it was found that there was about 3.13 ± 0.01% by weight amount of the ATPP unreacted. As a result of that, the final mole ratio of the mixture was 1 TEOS: 22 EtOH: 5 H_2O: 0.004 HCl: 3.43 × 10^{-5} ATPP–Si.

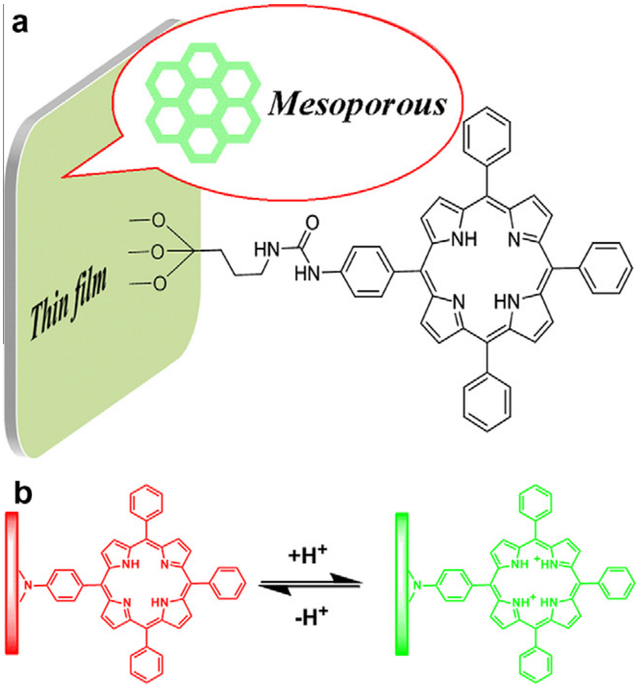
The IR absorption spectra were measured in the range of 400–4500 cm^{-1} on an FT-IR spectrophotometer (Model Bruker Vertex 70 FTIR) using KBr pellet technique. The UV–vis electronic absorption measurements were performed with a Shimadzu UV-3000 spectrophotometer. Films spin-coated on quartzes were used for UV–vis electronic absorption spectra measurements. ^{1}H NMR spectra were recorded on a Bruker AC 400 spectrometer. SAXRD patterns were recorded on a Philips PW 1710 diffractometer using Cu Kα1 radiation at a 0.02° (2θ) scanning step. The luminescent spectra of dried thin films were recorded by a Hitachi-4500 fluorescence spectrophotometer.

3. Results and discussion

The molecular structure of modified porphyrin used in this study is illustrated in Scheme 1a. The mesoporous characteristic of the films is established by the small angle X-ray diffraction patterns shown in Figure 1. For the resulting samples, only one typical diffraction peak indexed as (1 0 0) was detected for each film, indicating the formation of bicontinuous worm-like mesostructure within the silica films [23,26]. Owing to the pore shrinkage during extraction in the acid ethanol solution, the resulted film exhibits the same mesoporous characteristics with that of the as-deposited film with some slight shift. The formation of urea bond is confirmed by FTIR spectra shown in Figure 2. The FTIR spectrum of ATPP–Si is dominated by υ_{as}(Si–CH_2, 1165 cm^{-1}) and υ_{as}(Si–OEt, 1076 cm^{-1}) absorption bonds, showing the characteristic of hydrolysable trialkoxylsilyl moieties. The successful formation of urea group (NH–CO–NH) is confirmed by the appearance of aborption peaks at 1695, 1649, 1595 and 1537 cm^{-1} and the absence of the NH strectch bond at 1616 cm^{-1}, as shown in Figure 2.

Porphyrin can transfer its structure from protonated state (H_4TPP^{2+}), which is defined as state ‘0’ , to neutral state (H_2TPP), which is defined as state ‘1’, upon various pH values, as depicted in Scheme 1b. From Figure 3, it can be seen that both absorption and emission spectroscopic variations accompanied with this state transformation process, the absorption peak at 416 nm and the presence of the emission peak at 646 nm for state ‘1’ (H_4TPP^{2+}), and the absorption peak at 444 nm and the absence of the emission peak at 646 nm for state ‘0’ (H_2TPP).Based on this variations of the absorption property of the porphyrin complex, sequential logic operations can be accomplished and further discussed.

The porphyrin, owing to the introduction of acid (HCl) during mesoporous film preparated, is protonated and turned out to be H_4TPP^{2+}. And the initial state is thus fixed to be state ‘0’



Scheme 1. a. The structure of porphyrin used in this study and b. the alternative structures of porphyrin under base (red) or acid (green) condition.

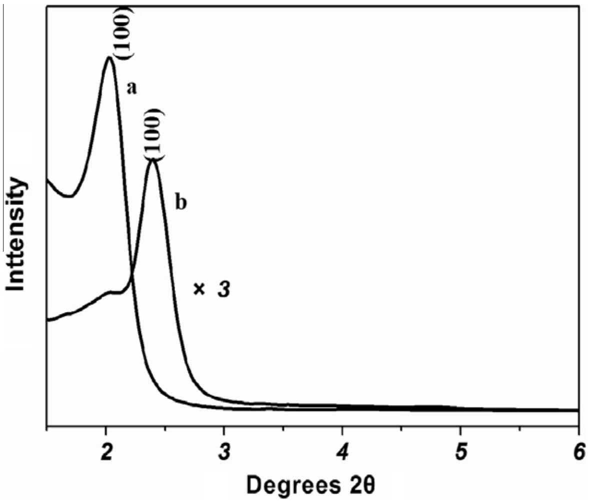


Figure 1. XRD patterns of the as-deposited film (a) and the film after (b).

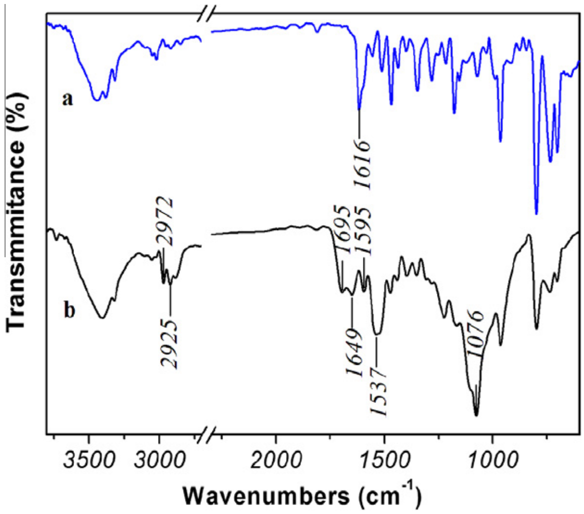


Figure 2. FT-IR spectra of porphyrin (a) and the siliane porphyrin (b).

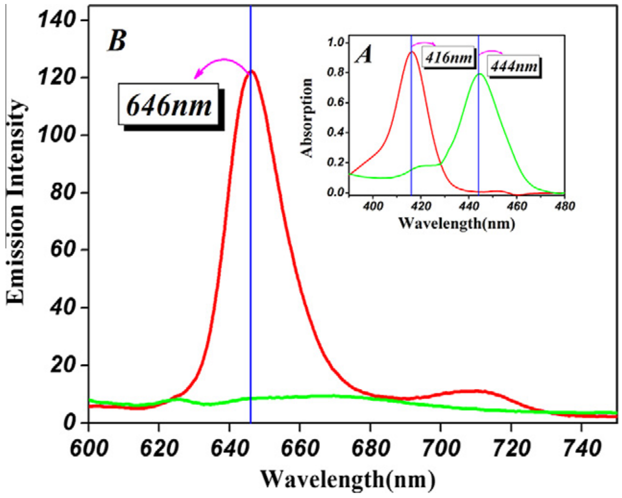


Figure 3. The absorption spectra (A) and the emission spectra (B) of the neutral (red curve) and the protonated (green curve) porphyrin.

(H_4TPP^{2+}). In order to depict the processes of RS-latch and feedback loop clearly, the state of the porphyrin should be written to state ‘1’.

3.1. One input feedback loop

For further research effort, the neutral porphyrin (H_2TPP) state ‘1’ is defined as the initial state of this system. While, interacting with acid (H^+) or not corresponds to the input of ‘1’ or ‘0’, and the presence or absence of the porphyrin absorption peak at 416 nm is defined as the output of ‘1’ or ‘0’, respectively. The film is dipped in 0.01 mol/L HCl in ethanol solution for 5 min, followed by washing with absolute ethanol and deionized water for several times, and dried by flowing N_2. Since the loading level of the porphyrin (the mole ratio of ATPP–Si to final SiO_2 is 3.43×10^{-5}) in the film is far more lower than the molar concentration of input acid or base and the porphyrin is loaded in the mesoporous structure which is benefit for interacting between the response material and input, and also for removing trace of the old input residual with the new input, the porhyrin would be fully protonized or deprotonized during the operation. Only when H^+ is present and the system is in state ‘1’ (H_2TPP), can the film change to state ‘0’ (H_4TPP^{2+}) whose absorption peak at 416 nm is red-shift to 444 nm corresponding to state ‘0’ (H_2TPP). The state ‘0’ (H_2TPP) was stored at the moment when the film interacted with acid to form state ‘0’, even though it was taken out from the acid solution and washed by ethanol and deionized water, and couldn’t be changed by further additional interacting with acid. The corresponding truth table of that mentioned logic is shown in Table 1.

As for H_4TPP^{2+}, the current state of porphyrin could be stored and feedback to the next state, interacting with new inputs. In a sense, it could be briefly considered as a one-bit random (RAM) cell. [20] For further application, a storage device with the major function of data memory will be achieved by integrating these cells together to form a regular array. The data will be written by introducing acid to part of the array. Simultaneously, the absorption peak at 444 nm of porphyrin could also be obviously used as another detector for this feedback loop as mentioned, with base as its input.

3.2. Two input RS latch

As mentioned, once interacting with acid, the state of this film is held to state ‘0’ (H_4TPP^{2+}), even though the input acid was absolutely washed away. In order to obtain state ‘1’, the film is dipped in 0.01 mol/L NaOH in THF solution for 5 min. After that the film is washed by absolute ethanol and deionized water for several times followed by drying in flowing N_2 at room temperature. The absorption peak is blue shift from 444 nm to 416 nm, accompanied by the emission at 646 nm excited by light at 420 nm. Until base was introduced to interact with the film, this system could not be turned to state ‘1’ (H_2TPP). It is defined as Set operation.

After previously processed by base and detection, the film is immediately dipped in acid solution as mentioned for 5 min to gain state ‘0’ (H_4TPP^{2+}). Its absorption peak is red shift back to 444 nm

Table 1
The truth table of feedback-loop with different current states and one input: H^+; output: Absorption (416 nm).

Entry	In H^+	Current state	Next state	Output
1	0	1	1	1
2	1	1	0	0
3	0	0	0	0
4	1	0	0	0

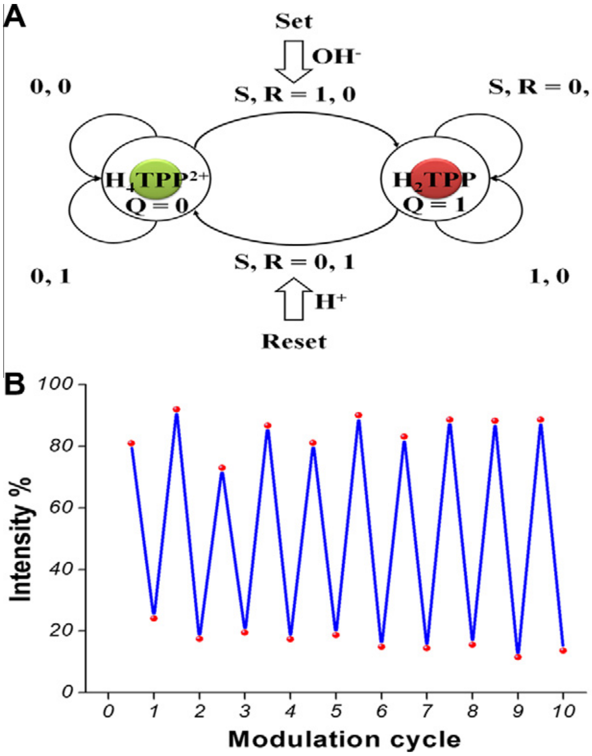


Figure 4. (A) State diagram of this system: three different R, S input conditions acting with the two possible current states $Q = 0$ and 1 of the porphyrin device. Remark that R, $S = 1$, 1 is not allowed; (B) cycle test on the vibration of absorption intensity between the two states of the neutral (upper points) and protonated (lower points) porphyrin as the function of cyclic numbers.

Table 2
The truth table of RS-latch with two chemical inputs: Set: OH^- and Reset: H^+ ; output: Q: Absorption (416 nm) and $\overline{Q}$: Absorption (444 nm).

Entry	Input		Current state	Next state	Output	
	S	R			Q	$\overline{Q}$
1	0	0	1	1	1	0
2	0	1	1	0	0	1
3	0	0	0	0	0	1
4	0	1	0	0	0	1
5	1	0	0	1	1	0
6	1	0	1	1	1	0

accompanied by the absence of emission peak at 646 nm. It is defined as Reset operation. As a result of that, once the state is set (reset) to state '1' (state '0'), it couldn't be turned back to state '0' (state '1') until acid (base) is added.

Consequently, it could be reasonably described as a RS-latch and defined as follows: (1) two inputs: Set (OH^-) and Reset (H^+); (2) two outputs of Q: the presence of the absorption peak at 416 nm and $\overline{Q}$: the presence of the absorption peak at 444 nm from porphyrin. The RS-latch operation is depicted as follows: WRITE, as the Set input is predominant, state '1' (H_2TPP) is recorded and preserved; ERASE, alternatively, state '1' is erased by high impulse of Reset input and replaced as state '0' (H_4TPP^{2+}). For the RS-latch in the system of conventional logic circuit, it's remarkable to notice that the two inputs can't be fixed to '1' at the same time.[14–18,20] The state diagram and truth table of that mentioned logic are illustrated in Figure 4A and Table 2.

The cycle test has been carried out to ensure its stability and reliability by detecting the absorption peak at 416 nm. In Figure 4B, it's shown that after a few cycles the absorption intensity maintains at merely the same level for both limits of the system due to the ordered mesostructure which is advantageous to the interaction between input chemicals and porphyrin. Along with increasing number of test cycles, the intensity of absorption is heightened to a relative balanced level rather than weakened. It further demonstrates that the porphyrin would not be washed away with inputs during washing operation.

4. Conclusion

Asymmetric 5-(4-aminophenyl)-10, 15, 20-triphenyl-porphyrin (H_2ATPP) is covalently bonded to mesoporous thin films. Using its characteristic of being sensitive to acid–base reflected in its spectra, sequential logic is achieved by taking account of different inputs and outputs. By providing large surface area, the mesoporous film is not only benefit for the fully interacting between porphyrin and acid or base, but also for fully washing away chemical inputs without changing states and porphyrin lost. Further research is being carried out to achieve integrated logic at molecular level to accomplish practical function molecular devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.06.002.

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