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Logic Gates

# Highly Sensitive INHIBIT and XOR Logic Gates Based on ICT and ACQ Emission Switching of a Porphyrin Derivative**

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**Abstract:** Fluorescence-switch-based logic devices are very sensitive compared with most of the reported devices based on UV/Vis absorption systems. Herein, we demonstrate that a simple molecule, 5,10,15,20-tetra-(4-aminophenyl)porphyrin (TAPP), shows protonation-induced multiple emission switches through intramolecular charge transfer and/or aggregation-caused quenching. Highly sensitive INHIBIT and XOR logic gates can be achieved by combining the intermolecular assembly with the intramolecular photoswitching of diprotonated TAPP ($TAPPH_2^{2+}$). In addition, molecular simulations have been performed by DFT for a better understanding of the emission-switching processes.

Molecular logic has experienced a boost in popularity since the introduction of the first AND gate in solution by de Silva et al. in 1993.[1] From then on, most of the common logic operations have been derived from switchable molecular systems,[2] such as OR,[3] XOR,[4] NOR,[5] NAND,[6] and INHIBIT.[7] Among them, the XOR gate is a digital logic gate with two or more inputs and one output that performs exclusive disjunction, whereas the INHIBIT gate produces a certain or fixed output whatever the inputs might be or even when the input changes. In fact, the outputs typically rely on photonic processes of UV/Vis absorption and emission.[8] Especially, fluorescent output has attracted much attention due to its high sensitivity. "On" and "off" fluorescence are referred to as the binary digitals "1" and "0", respectively. In general, the fluorescent sensitivity highly depends on the "on"/"off" ratio, for which the optimal result is absolute quenching.[9] Therefore, the search for pathways that weaken the emission is extremely necessary and crucial.

It is possible to control emission by designing a versatile molecule with at least one fluorophore–spacer–receptor segment, which sustains the emission-switching processes,[10] such as photoinduced electron transfer (PET),[11] intramolecular charge transfer (ICT),[12] twisted intramolecular charge transfer (TICT),[13] and resonance energy transfer (FRET).[14] A molecule with two or more switching processes is supposed to be beneficial for increasing the signal diversity. For example, Akkaya and co-workers reported effective PET and ICT emission switching for a molecular half-subtractor in 2005.[15] Later, they widened the applications of styryl–boron-dipyrromethene (bodipy) derivatives in molecular logic and fluorescence sensing by selective manipulation of ICT and PET processes.[16] Chemosensors, which combine those two or more processes, have attracted much attention as well.[17] However, the molecular complexity increases with the introduction of more intermolecular quenching processes, that is, an increasing number of spacers and receptors. Extended π systems with strong emission, except in aggregated states, carry out quenching process through aggregation-caused quenching (ACQ).[18] As Xu et al. reported, molecular flattening can be an efficient quenching pathway for π–π cooperative interactions between 2D graphene layers and the large π system of porphyrin molecules.[19] Accordingly, designing a simple molecule through intermolecular assembly can perhaps produce diversiform signals through only one intramolecular process. Nonetheless, little attention has been paid to this type of combinational work.

Porphyrins, which are perfect emissive molecules, quench fluorescence by forming assemblies through π–π interactions and hydrophobic effects. Emission is observed when the assembled structures disperse. Therefore, porphyrins are actually appropriate candidates for combining ACQ with an intramolecular process.[20] The core N atoms of 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP, Scheme S1 and Figure S1 in the Supporting Information) can be primarily protonated,[8b] and thus TAPP changes into $TAPPH_2^{2+}$, which is regarded as an amphophilic molecule for both trapping and releasing $H^+$.[21] Herein, we report the fluorescent switch of INHIBIT and XOR logic gates based on $TAPPH_2^{2+}$ by ICT and ACQ processes by using $H^+$ and $OH^-$ as inputs (Scheme 1). Fluorescence quenching results from the first conjoined use of intramolecular interaction and intermolecular assembly. In addition, it is also the first report on a "turn-on" fluorescence approach for TAPP under strong acidic, aqueous conditions, and hence TAPP may be used as an emission sensor at low pH values.

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[**] ICT = intramolecular charge transfer; ACQ = aggregation-caused quenching.

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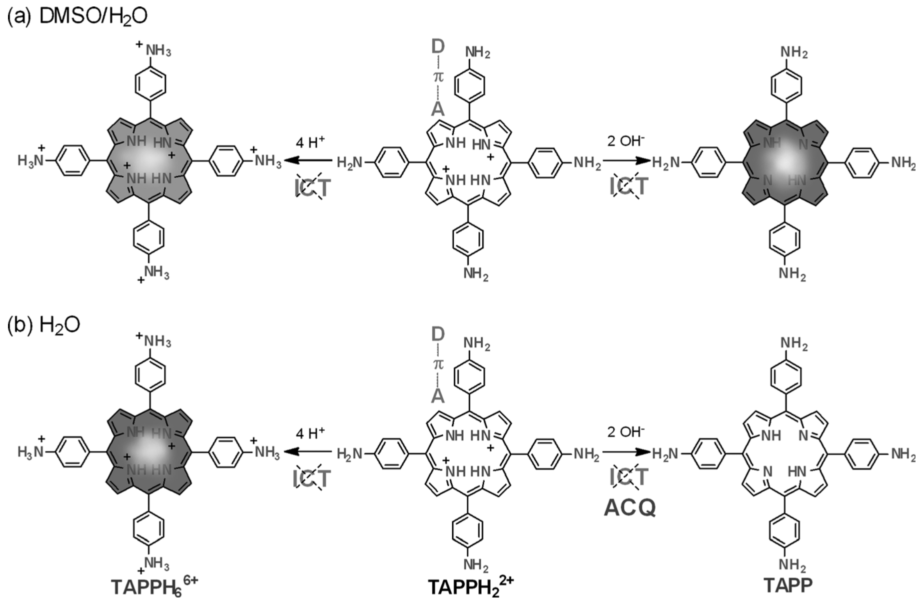

**Scheme 1.** Schematic illustration of the emission change with protonation of TAPP in a) DMSO/$H_2O$ (1:1) or b) $H_2O$.

Figure 1 a shows the UV/Vis absorption spectra of TAPP in DMSO/$H_2O$ (1:1) at different pH values (for different concentrations of TAPP, see Figure S2, and for solvent ratios, Figure S3 in the Supporting Information). $TAPPH_2^{2+}$ can be generated in acidic media. Further protonation of peripheral amino groups is more difficult, and a strong acidification is needed to allow spectroscopic observation of $TAPPH_6^{6+}$. The electronic absorption spectra of TAPP exhibit two transformations. Redshift of the Soret band ($\lambda_{max}=432$ nm) is observed by 36 nm by lowering the pH value from 6 to 3, followed by a blueshift with the pH change from 2.8 to 0 ($\lambda_{max}=439$ nm; Figure 1 a). The UV/Vis spectra are in accordance with previous work reported by Weinkauf et al.[22] Compared with an "on" fluorescence in dichloromethane and quenched fluorescence in DMSO, the fluorescence of TAPP quenches step by step along with the increasing concentration of $H^+$ in DMSO/$H_2O$ (Figure 1 b). Inner N atoms as electronrich units transform to electronpoor atoms when TAPP is protonated under acidic conditions; this contributes to the formation of the D–π–A structure. In this regard, the $TAPPH_2^{2+}$ emission should be quenched in polar solvents, such as our aqueous system. Surprisingly, the emission of our system turns on when the pH is low enough (pH < 1; Figure 1 b), which has never been reported before. From the point view of the molecular structure, the D–π–A structure can be destroyed by the protonation of periphery amino groups. Thus $TAPPH_6^{6+}$ represents "on" fluorescence even in highly polar solvents. The three protonation states result in an "on–off–on" emission process in DMSO/$H_2O$.

Theoretical calculations were performed with DFT at the B3LYP/6-31G basis level in the Gaussian 03 B.02 package to better understand the emissive properties of TAPP at different levels of protonation.[23] The simulation results are shown in Figure 2, including the optimized molecular configuration and electron distributions of the HOMO and LOMO of $TAPPH_6^{6+}$, $TAPPH_2^{2+}$, and TAPP. The electron clouds of both the HOMO and LOMO are mainly located on the central porphyrin core of TAPP. This result suggests that the optical transition from the LUMO to the HOMO is direct, and there is no ICT from the peripheral amines to the porphyrin core.[24] It can be used to explain why high fluorescence can be monitored even in highly polar solvents. In sharp contrast, the HOMO and LUMO of $TAPPH_2^{2+}$ are mainly distributed along the terminal phenyl units and the central porphyrin core, respectively. Therefore, an obvious ICT is anticipated for $TAPPH_2^{2+}$. This has been confirmed by the fluorescent behavior in solutions with different polarities, for example, in aqueous and in DMSO systems. The orbital distribution also agrees with our explanation for $TAPPH_6^{6+}$ with a weak ICT. We also investigated the fluorescence of other species with different extents of protonation by theoretical calculations (Figure S4 and S5 in the Supporting Information). Surprisingly, the results show that the fluorescence of $TAPPH_5^{5+}$, without ICT, can also be "on" in aqueous solutions. In short, the theoretical results coincide with the "on–off–on" emission process in DMSO/$H_2O$.

Similar to that measured in DMSO/$H_2O$, the UV/Vis absorption spectra in $H_2O$ exhibit a redshift, followed by a blueshift, with different absorption densities (Figure 1 c). There is still a "turn-on" emission at extremely low pH values. Moreover, the fluorescence intensity that results from strong acidification of the $H_2O$ solution exceeds that in DMSO/$H_2O$ (1:1). Figure 1 b and d show "turn-on" fluorescence at pH 1.0 and pH 2.8, respectively, proving the formation of $TAPPH_6^{6+}$. Nevertheless, the emission is absolutely quenched in near neutral $H_2O$ (Figure 1 d). The TAPP molecules aggregate because of π–π interactions and hydrophobic effects, similarly to tetraarylporphyrin in $H_2O$.[25] At lower pH values, TAPP shows an "off–on" emission process (Scheme 1 b). Therefore, in contrast to the process in DMSO/$H_2O$, the "off–on" emission process in $H_2O$ can be explained by adding ACQ.

Interestingly, the fluorescence responses of $TAPPH_2^{2+}$ to different combinations of $H^+$ and $OH^-$ constitute an INHIBIT gate in $H_2O$ and an XOR gate in DMSO/$H_2O$ (Figure 3). It is difficult to implement an XOR gate in a chemical system, because the responses to two different stimuli are complex.[2a] Figure 3 a signifies the "turn-on" fluorescence at pH 0 and 14, but also the "off" state at pH 3.0 (for UV/Vis adsorption spectra and fluorescence spectra at pH 0 to 14, see Figure S6–S7 in the Supporting Information). By contrast, the INHIBIT gate is a two-input AND gate with a one-input NOT gate (Figure 3 b). This is realized through the "turn-on" emission process of TAPP in

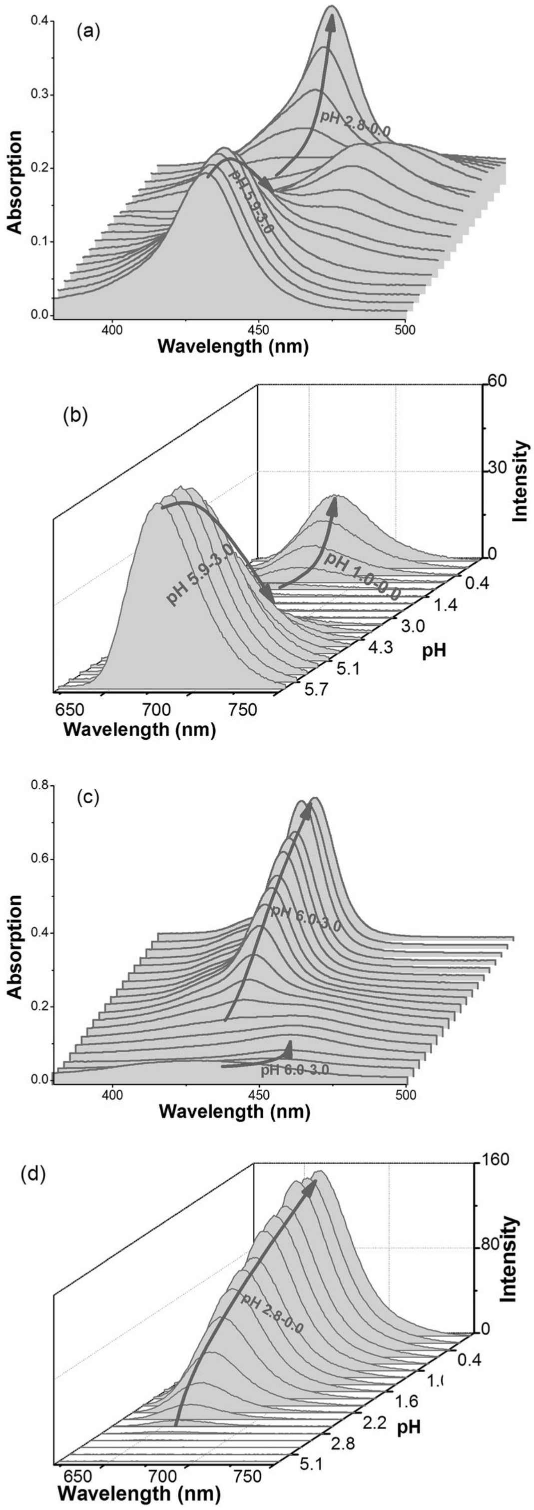

**Figure 1.** a) UV/Vis absorption spectra and b) fluorescence spectra of TAPP (1 $\mu$M) in DMSO/$H_2O$ (1:1) at different pH values ($\lambda_{max} = 439$ nm). c) UV/Vis absorption spectra and d) fluorescence spectra of TAPP (1 $\mu$M) in $H_2O$ at different pH values ($\lambda_{max} = 432$ nm).

$H_2O$ at different pH values. Importantly, the high sensitivity of INHIBIT and XOR logic gates are achieved through fluorescent switch processes. Also by virtue of emission switches, TAPP can be used as a fluorescent sensor at pH 0–6 (Figure S8 in the Supporting Information).

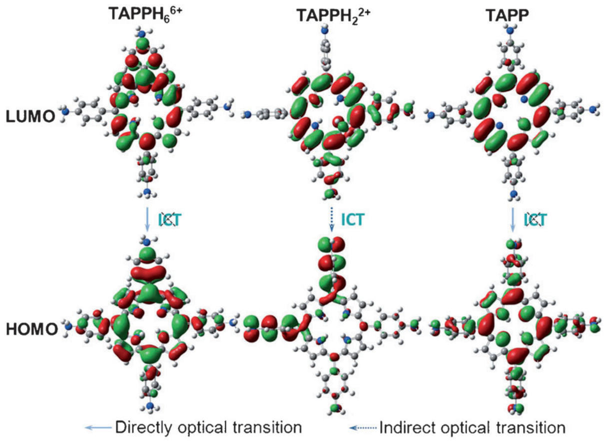

**Figure 2.** LUMO and HOMO of TAPP, $TAPPH_2^{2+}$ and $TAPPH_6^{6+}$ in optimized structures obtained by Gaussian 03, B3LYP/6-31G basis set.

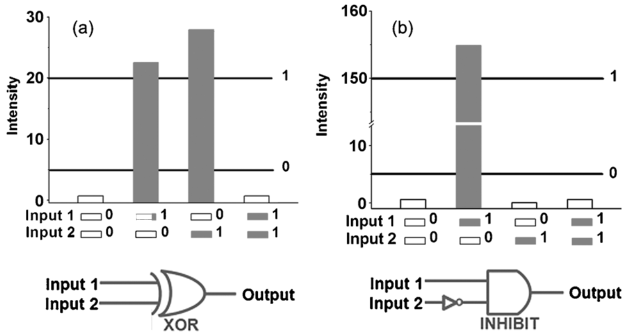

**Figure 3.** Output and the corresponding truth tables for the a) XOR ($\lambda_{ex} = 439$ nm) and b) INHIBIT gates ($\lambda_{ex} = 432$ nm) of $TAPPH_2^{2+}$ using $H^+$ (Input 1) and $OH^-$ (Input 2). The solid line indicates the detection limit.

In summary, we mainly focus on the combination of intra- and intermolecular interactions to achieve logic-based devices, by first demonstrating the continuous fluorescent conversion of TAPP in different aqueous systems. As fluorescent switch-type logic gates, the revealed INHIBIT and XOR gates are instinctively highly sensitive. Furthermore, TAPP can be used as an alert sensor in very acidic conditions as a consequence of the "turn-on" fluorescence of TAPP in aqueous systems with low pH values. Additionally, coupling the intramolecular switch to intermolecular assembly simplifies the design of logic molecules, and is a promising method to be extended to other types of emission systems, such as multiple chemical passwords,[26] dual-analytic Luciferin Imaging,[27] and the detection by emission color change.[28]

## *Acknowledgements*

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**Keywords:** ACQ · emission switching · ICT · logic gates · porphyrins

[1] P. A. de Silva, N. H. Q. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42–44.

[2] a) K. Szaciłowski, *Chem. Rev.* **2008**, *108*, 3481–3548; b) U. Pischel, J. Andréasson, D. Gust, V. F. Pais, *ChemPhysChem* **2013**, *14*, 28–46; c) Y. Ding, X. Li, J. P. Hill, K. Ariga, H. Ågren, J. Andréasson, W. Zhu, H. Tian, Y. Xie, *Chem. Eur. J.* **2014**, *20*, 12910–12916.

[3] F. Pu, E. Ju, J. Ren, X. Qu, *Adv. Mater.* **2014**, *26*, 1111–1117.

[4] A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart, *J. Am. Chem. Soc.* **1997**, *119*, 2679–2681.

[5] A. P. de Silva, I. M. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell, T. E. Rice, *J. Am. Chem. Soc.* **1999**, *121*, 1393–1394.

[6] H. T. Baytekin, E. U. Akkaya, *Org. Lett.* **2000**, *2*, 1725–1727.

[7] H. Miyaji, H.-K. Kim, E.-K. Sim, C.-K. Lee, W.-S. Cho, J. L. Sessler, C.-H. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 12510–12512.

[8] a) R. Gotor, A. M. Costero, S. Gil, M. Parra, P. Gavina, K. Rurack, *Chem. Commun.* **2013**, *49*, 11056–11058; b) S. J. Langford, T. Yann, *J. Am. Chem. Soc.* **2003**, *125*, 11198–11199.

[9] A. Ding, L. Yang, Y. Zhang, G. Zhang, L. Kong, X. Zhang, Y. Tian, X. Tao, J. Yang, *Chem. Eur. J.* **2014**, *20*, 12215–12222.

[10] a) A. P. de Silva, T. P. Vance, M. E. S. West, G. D. Wright, *Org. Biomol. Chem.* **2008**, *6*, 2468–2480; b) B. Maerz, S. Wiedbrauk, S. Oesterling, E. Samoylova, A. Nenov, P. Mayer, R. de Vivie-Riedle, W. Zinth, H. Dube, *Chem. Eur. J.* **2014**, *20*, 13984–13992.

[11] a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; b) A. J. M. Huxley, M. Schroeder, H. Q. Nimal Gunaratne, A. P. de Silva, *Angew. Chem. Int. Ed.* **2014**, *53*, 3622–3625; *Angew. Chem.* **2014**, *126*, 3696–3699.

[12] Y. Li, T. Liu, H. Liu, M.-Z. Tian, Y. Li, *Acc. Chem. Res.* **2014**, *47*, 1186–1198.

[13] N. Amdursky, Y. Erez, D. Huppert, *Acc. Chem. Res.* **2012**, *45*, 1548–1557.

[14] W.-S. Li, M.-J. Teng, X.-R. Jia, B.-B. Wang, J.-M. Yeh, Y. Wei, *Tetrahedron Lett.* **2008**, *49*, 1988–1992.

[15] A. Coskun, E. Deniz, E. U. Akkaya, *Org. Lett.* **2005**, *7*, 5187–5189.

[16] O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci, E. U. Akkaya, *J. Am. Chem. Soc.* **2010**, *132*, 8029–8036.

[17] a) P. G. Sutariya, A. Pandya, A. Lodha, S. K. Menon, *Analyst* **2013**, *138*, 2531–2535; b) X. Lu, W. Zhu, Y. Xie, X. Li, Y. Gao, F. Li, H. Tian, *Chem. Eur. J.* **2010**, *16*, 8355–8364; c) N. I. Georgiev, A. M. Asiri, A. H. Qusti, K. A. Alamry, V. B. Bojinov, *Dyes Pigm.* **2014**, *102*, 35–45.

[18] J. Xu, X. Liu, J. Lv, M. Zhu, C. Huang, W. Zhou, X. Yin, H. Liu, Y. Li, J. Ye, *Langmuir* **2008**, *24*, 4231–4237.

[19] Y. Xu, L. Zhao, H. Bai, W. Hong, C. Li, G. Shi, *J. Am. Chem. Soc.* **2009**, *131*, 13490–13497.

[20] Z. Chen, A. Lohr, C. R. Saha-Moller, F. Wurthner, *Chem. Soc. Rev.* **2009**, *38*, 564–584.

[21] E. C. A. Ojadi, H. Linschitz, M. Gouterman, R. I. Walter, J. S. Lindsey, R. W. Wagner, P. R. Droupadi, W. Wang, *J. Phys. Chem.* **1993**, *97*, 13192–13197.

[22] J. R. Weinkauf, S. W. Cooper, A. Schweiger, C. C. Wamser, *J. Phys. Chem. A* **2002**, *107*, 3486–3496.

[23] Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[24] X. Y. Shen, Y. J. Wang, E. Zhao, W. Z. Yuan, Y. Liu, P. Lu, A. Qin, Y. Ma, J. Z. Sun, B. Z. Tang, *J. Phys. Chem. C* **2013**, *117*, 7334–7347.

[25] J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, UK, **1970**.

[26] B. Rout, P. Milko, M. A. Iron, L. Motiei, D. Margulies, *J. Am. Chem. Soc.* **2013**, *135*, 15330–15333.

[27] G. C. Van de Bittner, C. R. Bertozzi, C. J. Chang, *J. Am. Chem. Soc.* **2013**, *135*, 1783–1795.

[28] D. Kim, T. S. Lee, *Chem. Commun.* **2014**, *50*, 5833–5836.

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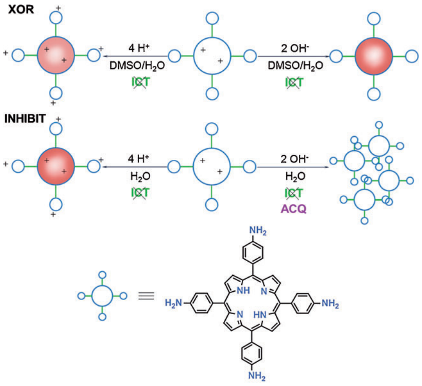
## COMMUNICATION

**Molecular logic**: 5,10,15,20-Tetra-(4-aminophenyl)porphyrin with intermolecular assembly abilities shows multiple emission switches and produces diversiform logic signals of high sensitivity by combining intermolecular assembly with intramolecular photoswitching (see figure). In addition, DFT helps to further understand of the emission switching processes. (ICT = intramolecular charge transfer; ACQ = aggregation-caused quenching.)



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