New TTF derivatives: several molecular logic gates based on their switchable fluorescent emissions†

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The new redox-fluorescence dependent molecules MTs were synthesized with tetrathiafulvalene (TTF) and 5-methoxy-2-pyridylthiazoles coupled directly and rigidly. The fluorescent emission of MTs can be reversibly switched on/off depending on the oxidation states of the TTF unit, due to the peculiar property of TTF being oxidized reversibly and selectively. The dicationic MTs display a strong emission in the visible region and can be quenched by various chemical inputs. Based on this switchable fluorescent property of MTs, several logic gates such as AND, OR, NOT, NOR, INHIBIT, XNOR and NAND were realized by purposely selecting the initial states and chemical inputs.

Introduction

As an excellent electron donor, tetrathiafulvalene (TTF) and its derivatives have been investigated extensively,[1] especially for the development of organic conducting materials.[2] Many versatile applications of this renown electron donor unit in a wide range of research areas have been demonstrated,[3–7] including electrical,[8] magnetic,[9] and optical materials.[1] Therefore, TTF and its derivatives have proven to be promising candidates for the investigation of the photoinduced electron-transfer (PET) process and long-lived charge-separated states.[10]

Donor–acceptor molecules containing TTF units have been studied as models for fundamental investigation of electron/charge transfer interactions based on the unique property of the TTF unit that can be reversibly transformed to the corresponding cation radical ($TTF^{\bullet +}$) and dication (TTF^{2+}) by either chemical or electrochemical oxidation at easily accessible potential windows.[1,2] It is well-known that the redox characteristic of the TTF unit can induce quenching of the emission of signaling subunits such as anthracene, naphthalene, and pyrene *via* a PET process,[11] and the signal generation strategy based on binding modulated donor–acceptor distance has successfully been employed in the development of biosensors.[12]

Logic gates are switches whose output state (0 or 1) depends on the input condition (0 or 1). It would be possible to extend the information processing and computation to the molecular level if only molecular logic gates were available, which could perform binary arithmetic and logical operations.[13] Therefore, the mimicry of elementary functions of complex logic operations at the molecular scale is of great scientific interest, since it introduces new concepts in the field of chemistry and stimulates the ingenuity of the research workers engaged in the bottom-up approaches.[14] Although computation at the molecular level appears to be far off,[15] the design and construction of molecular level systems capable of existing in different forms interconverted by external stimuli is interesting in both basic and applied research,[16] and many molecules that can exist in two forms interconvertable by an external input have been investigated. However, systems capable of existing in multistate (more than two forms) and that can be interconverted by more than one type of external stimulus, that is multifunctional, are less common.[17] Since de Silva and co-workers reported their pioneering work about molecular AND logic gates,[18] the design and construction of molecular systems capable of performing binary arithmetic and logical operations have been explored extensively.[19–21]

Herein we report new TTF derivatives 2-[4-(2,2′-bi-1,3-dithiol-4-yl)-5-methoxy-1,3-thiazol-2-yl]pyridine (MTs) which contain a fluorophore 5-methoxy-2-pyridylthiazole (MPT) (Chart 1) prepared by our lab,[22] where the TTF moiety plays a role of redox-active switch unit in these new molecules, due to its reversible and selective transformation between the neutral state through the cationic radical and dicationic states. The molecules are fluorescent in their dicationic state, in which emission can be reversibly switched off/on in corresponding neutral, cationic and dicationic states. Based on this peculiar

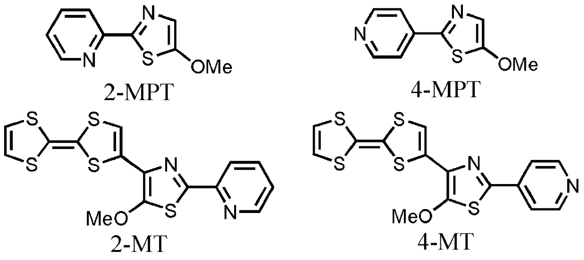

Chart 1 The structure of 2-MPT, 4-MPT, 2-MT, and 4-MT.

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property, several molecular gates, such as AND, OR, NOR, NOT, NAND, XNOR and INHIBIT(INH), have been constructed.

Experimental

Materials and methods

Tributyltinchloride, tetrakis(triphenylphosphine)palladium, $NOBF_4$, *N*-iodosuccinate (NIS) and LDA from Acros and Sigma-Aldrich, and trifluoroacetic acid from Alfa Aesar were used as purchased without further purification. The other chemicals were of AR grade and used as received. The solvents used were purified with standard methods prior to use. All reactions requiring anhydrous condition were conducted with the standard Schlenk technique.

Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. NMR spectra were recorded on a BRUKER ARX 400 spectrometer with trimethylsilane (TMS) as the internal standard. High resolution mass spectra were measured on a Micromass ZAB-HS spectrometer. Cyclic voltammetry investigation was performed on a CHI-840 Electrochemistry work station in a conventional three-compartment cell (1.0×10^{-2} M Bu_4NPF_6 as supporting electrolyte) at a scan rate of 100 mV s^{-1}. Solvent was dried and deoxygenated before used. A Pt disk was used as working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. UV-Vis absorption spectra were measured with a Shimadzu UV-3100 spectrophotometer and fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis

MPTs were synthesized as in our previous work,[22] and Bu_3Sn-substituted TTF (TTF-$SnBu_3$) was prepared according to the literature.[23] MTs were prepared through 4-iodo-5-methoxy-2-pyridylthiazole (IMPT) coupled with TTF-$SnBu_3$ in toluene (Scheme 1).

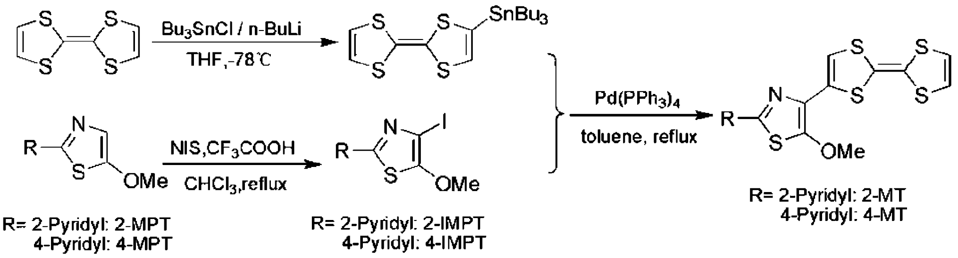
2-MT. The Typical two-step procedure is described with 2-MT: the mixture of 2-MPT (0.90 g), NIS (1.2 g), trifluoroacetic acid, and glacial acetic acid was refluxing for 5 h, and the cooled resulting mixture was added dropwise into the dichloromethane solution of triethylamine (50 mL). After the dichloromethane and unreacted triethylamine were removed under reduced pressure, the solution was diluted with water, and extracted with dichloromethane. The pure white solid, 4-iodo-5-methoxy-2-(2-pyridyl)-thiazole (2-IMPT), was obtained with chromatography on silica gel with ethyl acetate–CH_2Cl_2-petroleum ether as eluent. Yield: 1.3 g (87%). Then, the mixture of 2-IMPT (102 mg), TTF-$SnBu_3$ (159 mg) and $Pd(PPh_3)_4$ (37 mg) in toluene was refluxing for 12 h and annealed with water. Extracted with ethyl acetate, the solid thus obtained was purified with chromatography on silica gel with ethyl acetate–CH_2Cl_2–petroleum ether as eluent. Yield: 73 mg (58%). ^1H NMR (400 MHz, CF_3COOD) δ = 4.22 (s, 3H), 6.92 (s, 1H,), 7.84 (t, 1H), 8.05 (d, 1H), 8.50 (t, 1H), 8.64 (d, 1H), 8.90 (s, 2H); ^{13}C NMR (400 MHz, CF_3COOD) δ = 162.6, 147.9, 143.3, 142.3, 141.2, 137.6, 131.5, 125.6, 124.5, 122.7, 113.4, 112.4, 64.5; IR (KBr): 3055, 2924, 2853, 1493, 1434, 1336, 1004, 775 cm^{-1}; HR EI-MS, *m/z* (%): 392.97605 (100) $[M^+]$; Elemental analysis: $C_{15}H_{10}N_2OS_5$, Calc.: N, 7.10, C, 45.66, H, 2.55; Found: N, 6.42, C, 45.94, H, 3.00%.

4-MT. Yield: (58%). ^1H NMR (400 MHz, DMSO-d_6) δ = 4.17 (s, 1H), 6.75 (s, 1H), 7.12 (s, 1H), 7.75 (q, 2H), 8.67 (q, 2H); ^{13}C NMR (400 MHz, DMSO-d_6) δ = 160.0, 151.2, 149.1, 139.8, 129.4, 127.8, 120.7, 120.5, 119.5, 116.4, 110.9, 108.0, 65.5; IR (KBr): 3060, 2919, 2835, 1595, 1523, 1500, 1463, 1433, 1413, 1341, 1261, 1007, 762 cm^{-1}; HR EI-MS, *m/z* (%): 393.93874 (100) $[M^+]$; Elemental analysis: $C_{15}H_{10}N_2OS_5$, Calc.: N, 7.10, C, 45.66, H, 2.55; Found: N, 6.73, C, 45.35, H, 2.66%.

Results and discussion

Steady-state absorption spectra of 2-MT at different oxidation states in dichloromethane at room temperature are depicted in Fig. 1 (see also Fig. S1 and S2 for 4-MT†). The UV-visible spectrum of neutral 2-MT (Fig. 1) exhibits a characteristic absorption band of TTF at 385 nm. Upon addition of oxidative $NOBF_4$, the band at 385 nm gradually disappeared while a new band at 425 nm appeared with two shoulder peaks at 460 and 530 nm and a broad band in the range of 590 to 1150 nm, centered at 770 nm. Upon further oxidation with $NOBF_4$, the $TTF^{\bullet+}$ absorption at 770 nm and the shoulder peaks at 460 and 530 nm diminished, and the intensity of band at 425 nm decreased. In the meantime, a new band at 570 nm arose with the oxidation, which is assigned to the characteristic band of TTF^{2+} dication.[24] The observation of these changes of the electronic spectra suggests the oxidation occur at the TTF moiety in the present systems.

One of the most interesting properties of TTF is that it is possible to oxidize the TTF unit selectively and reversibly to form cation radical and dication species which can be



Scheme 1 Synthesis of 2-MT and 4-MT.

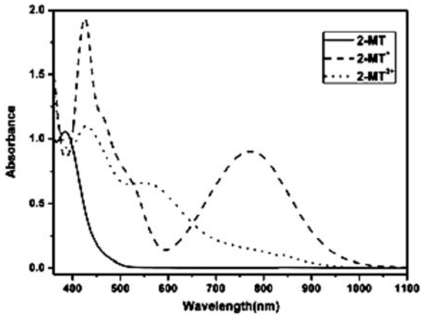


Fig. 1 Absorption of 1.0×10^{-4} M neutral, cationic and dicationic 2-MT in CH_2Cl_2 upon the addition of $NOBF_4$ in acetonitrile.

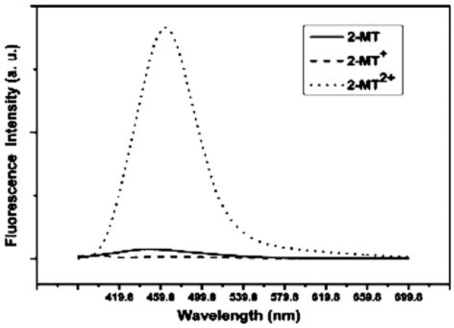


Fig. 2 The fluorescence spectra of 2-MT, $2\text{-MT}^{\bullet+}$, and 2-MT^{2+} in CH_2Cl_2.

monitored by the appearance of characteristic UV-visible absorption bands.[24,25] To study the reversibility of the processes in MTs, $NaBH_4$ was then added into the corresponding solution to reduce MTs^{2+} into $MTs^{\bullet+}$ and MTs species monitored by the appearance of corresponding characteristic UV-visible absorption bands at the cationic and neutral stages (see Fig. S2 and S3 in ESI†).

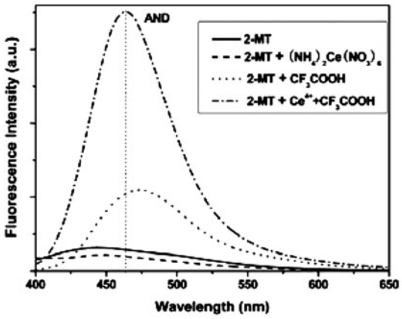
TTF displays a rich electrochemistry behavior, and the oxidation of its rings to the cation radical and dication species occurs sequentially and reversibly within a very accessible potential window.[1,2,26] Determination of the electrochemical behavior of MTs is important for evaluation of their potential to act as an electrochemical fluorescent switch. Electrochemical property of MTs was investigated by cyclic voltametry (CV) in dichloromethane at 1.0×10^{-4} M. Both 2-MT and 4-MT exhibit two reversible single-electron oxidative processes corresponding to the oxidation of TTF to $TTF^{\bullet+}$ and TTF^{2+} in different solvents, respectively (see Fig. S4 and S5 in ESI†). Compared with the electrochemical potentials of parent TTF ($E_1^{1/2} = 0.392$ V and $E_2^{1/2} = 0.775$ V, Ag/AgCl as reference electrode), the first oxidation potential of 2-MT at 0.315 V is obviously shifted cathodically by 77 mV, whereas the second oxidation potential 0.887 V is shifted anodically by 112 mV, indicating electron-donating from 2-MPT to TTF moiety, and therefore, an easier oxidation of TTF to $TTF^{\bullet+}$ in conjugation with 2-MPT, whereas in its dication form, TTF^{2+} could be an electron acceptor due to the decrease of electron density from the delocalization within the whole 2-MT molecular skeleton.

Fluorescence spectra were recorded in the visible region as shown in Fig. 2 (see also Fig. S6 in ESI†). The neutral MTs show a negligible fluorescence, while the dicationic MTs^{2+} display a very strong emission at 465 and 447 nm for 2-MT and 4-MT, respectively, upon excitation at 350 nm.

The experiments on fluorescence emission measurements coupled to chemical oxidation were carried out, since the TTF cation radical and dication species were achieved selectively with stoichiometric addition of oxidative reagent $NOBF_4$. To study the reversibility of the chemical redox process in 2-MT, $NaBH_4$ was then added to the corresponding solution to reduce 2-MT^{2+} into $2\text{-MT}^{\bullet+}$ and the 2-MT species were monitored by UV-visible absorption bands as mentioned above. Consequently, it is rational to conclude that the fluorescence of 2-MT can be reversibly modulated by the sequential chemical oxidation and reduction processes. Similar results were also observed for 4-MT.

Based on the distinct fluorescence properties of MTs among different states $MTs^{\bullet+}$ and MTs^{2+}, MTs can be operated within the molecule as the adjustable fluorescent "off–on" switches, which can be applied to construct various logic gates. In the present work, several molecular logic gates AND, NOT, OR, NOR, XNOR, NAND, and INHIBIT are realized with the fluorescence as the output signal. Although similar results can be obtained with both 2-MT and 4-MT (see Fig. S7 to S11 in ESI†), for simplicity, the description of these logic gate functions is based on 2-MT.

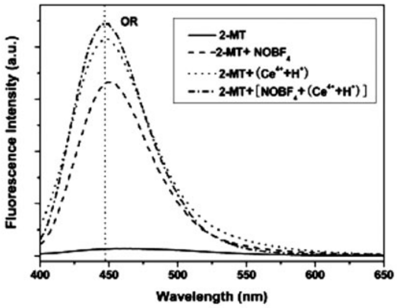
The experimental emission intensities and the truth table for an AND gate are shown in Fig. 3. To use 2-MT as a molecular AND gate, one input is defined as $(NH_4)_2Ce(NO_3)_6$ which provides the metal ion Ce^{4+}, and the other input is CF_3COOH. The molecule, dissolved in CH_2Cl_2, is initially set in the neutral state 2-MT without fluorescence. With neither input on, fluorescence output is below a threshold level (0.30), and the AND gate remains off. Protonation of 2-MT makes the molecule bright which displays an emission



The truth table for AND gate for 2-MT

Ce^{4+}	H^+	PL
0	0	0 (0.08)
1	0	0 (0.06)
0	1	0 (0.30)
1	1	1 (1.00)

Fig. 3 Fluorescence spectra of 5.0×10^{-5} M 2-MT in CH_2Cl_2 under different input conditions (5.0×10^{-5} M $(NH_4)_2Ce(NO_3)_6$ and 0.075 M CF_3COOH) and the truth table for AND logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.



The truth table for OR gate for 2-MT

$Ce^{4+} + H^+$	$NOBF_4$	PL
0	0	0 (0.03)
1	0	1 (0.92)
0	1	1 (0.74)
1	1	1 (1.00)

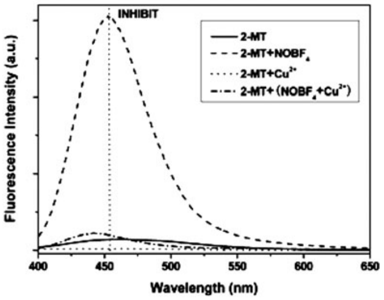
Fig. 4 Fluorescence emission spectra for 5.0 × 10^{-5} M 2-MT in CH_2Cl_2 under different input conditions (5.0 × 10^{-4} M $(NH_4)_2Ce(NO_3)_6$, 6.5 × 10^{-4} M CF_3COOH and 5 × 10^{-4} M $NOBF_4$) and the truth table for OR logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.

at 473 nm. With addition of H^+ from CF_3COOH, the fluorescence is thus triggered, resulting in the output of a weak fluorescence which is below the threshold. If input $(NH_4)_2Ce(NO_3)_6$ is applied, the fluorescence is quenched due to the ligation of Ce^{4+} with nitrogen, so the gate output remains off. Upon applying both inputs $(NH_4)_2Ce(NO_3)_6$ and CF_3COOH, a strong emission is observed, due to the appearance of fluorescent 2-MT^{2+} arising from the oxidation of 2-MT by Ce^{4+} in the acidic media. Thus, the molecule meets the criteria for an AND gate.

In contrast to the AND gate, the output of the OR gate is normally switched on if either one or both inputs are turned on. Starting with the neutral state of 2-MT, this molecule can perform as a molecular OR logic gate as shown in Fig. 4. 2-MT can be oxidized to fluorescent 2-MT^{2+}, which emits at 445 nm as an output, with the oxidative agent $NOBF_4$ or $(NH_4)_2Ce(NO_3)_6$ in acidic media CF_3COOH as an input. When $NOBF_4$ and $(NH_4)_2Ce(NO_3)_6$ in CF_3COOH were input simultaneously, the fluorescence of the dicationic 2-MT^{2+} at 445 nm is observed as an output, thus an OR logic gate was obtained when the output is read at 445 nm.

INHIBIT logic deserves some attention because it demonstrates a noncommutative behavior. This means that one input has the power to disable the whole system, that is, it holds a veto.[19] When 2-MT is used as an INHIBIT gate, the neutral state is set as initial state. Neutral 2-MT can be oxidized to the emissive dicationic 2-MT^{2+}, which comprises the fluorescent output of the gate. Input I_1 is the oxidative agent $NOBF_4$, generating 2-MT^{2+}, which is quenched by I_2 $Cu(ClO_4)_2$ and the gate is off. Thus, the requirements for an INHIBIT gate are met (Fig. 5).

Clearly, there is a long way to go to implement a practical application of a molecular computer. It is desirable to prepare systems capable of existing in different initial states which can interconverted by external stimulus, since this decreases the need for an additional processor. In the present system, the neutral state is set as initial state, and the AND, OR, and INHIBIT logic gate functions are carried out with MTs molecules. Keeping in mind the peculiar property of TTF to be oxidized selectively and reversibly to form cation radical and dication species and the fluorescent emission of MTs^{2+}, it is interesting to utilize the dicationic state as a different initial state to construct the other logic gates.



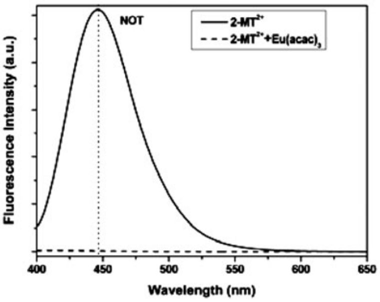
The truth table for INHIBIT gate for 2-MT

Cu^{2+}	$NOBF_4$	PL
0	0	0 (0.04)
1	0	0 (0.01)
0	1	1 (1.00)
1	1	0 (0.06)

Fig. 5 Fluorescence emission spectra for 5.0 × 10^{-5} M 2-MT in CH_2Cl_2 under different input conditions (5 × 10^{-4} M $NOBF_4$ and 1.0 × 10^{-3} M $Cu(ClO_4)_2$) and the truth table for INHIBIT logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.

NOT gate is a basic logic gate which contains only one input and an output and gate is usually turned off with an input. Starting with the dicationic fluorescent 2-MT^{2+}, the emission is quenched with the addition of $Eu(acac)_3$, thus a NOT logic gate is implemented (Fig. 6).

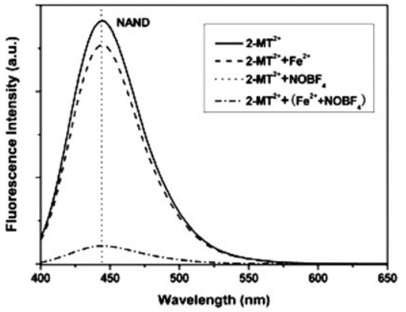
The NAND gate is particularly important; it is considered to be a universal gate, since every other gate function can be generated by successive implementation of NAND gates.[19,27] The experimental emission intensities and the truth table for a



The truth table for NOT gate for 2-MT

Eu^{3+}	PL
0	1 (1.00)
1	0 (0.00)

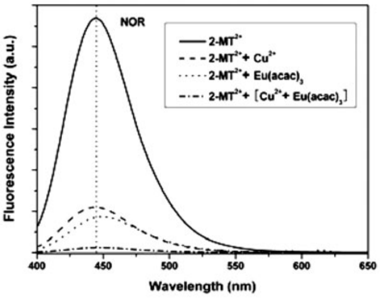
Fig. 6 Fluorescence emission spectra for 1.0 × 10^{-5} M 2-MT^{2+} in CH_2Cl_2 under different input conditions (5.0 × 10^{-4} M $Eu(acac)_3$) and the truth table for NOT logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.



The truth table for NAND gate for 2-MT

Fe^{2+}	$NOBF_4$	PL
0	0	1 (1.00)
1	0	1 (0.90)
0	1	1 (1.00)
1	1	0 (0.07)

Fig. 7 Fluorescence emission spectra for 5.0×10^{-5} M 2-MT^{2+} in CH_2Cl_2 under different input conditions (1.0×10^{-3} M $Fe(ClO_4)_2$ and 9.0×10^{-4} M $NOBF_4$) and the truth table for NAND logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.



The truth table for NOR gate for 2-MT

Cu^{2+}	Eu^{3+}	PL
0	0	1 (1.00)
1	0	0 (0.19)
0	1	0 (0.16)
1	1	0 (0.02)

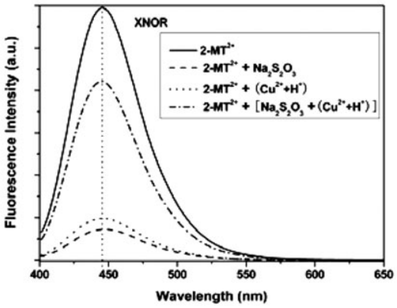
Fig. 8 Fluorescence emission spectra for 5.0×10^{-5} M 2-MT^{2+} in CH_2Cl_2 under different input conditions (1.0×10^{-3} M $Cu(ClO_4)_2$ and 1.0×10^{-3} M Eu(acac)$_3$) and the truth table for NOR logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.

NAND gate are shown in Fig. 7. The output, normally on, is switched off only if both inputs are turned on. Thus, NAND logic has an output of 1 for all combinations of binary inputs except where both inputs are turned on, a situation in which the output now becomes 0. In the absence of any inputs the excitation of the NAND gate at 350 nm results in fluorescence emission from the dicationic 2-MT^{2+}. Addition of either inputs Fe^{2+} or $NOBF_4$ individually has no effect on the emission and the fluorescent output of the gate remains high as output 1. Conversely, the presence of both Fe^{2+} and $NOBF_4$ inputs leads to fluorescence quench, which is due to the sequential quenching effect of Fe^{3+} from the oxidation of Fe^{2+} by $NOBF_4$. The resulting pattern of fluorescent output *versus* chemical inputs mimics that of an electronic NAND gate with a low output state (threshold < 0.1) occurring only in the presence of both inputs.

NOR gates, as well as NAND gates, have a high value in electronics, since multiple copies of these can be wired up to emulate all the other logic types.[27] The pattern of fluorescence intensity as a function of cation input is read as a NOR logic gate according to the truth table in Fig. 8. A NOR logic gate is achieved with Cu^{2+} and Eu^{3+} which do not quench the fluorescence completely. The output of fluorescence falls below the threshold value (< 0.2) upon addition of either Cu^{2+} or Eu^{3+}. Both Cu^{2+} and Eu^{3+} simultaneously supplied as inputs cause complete fluorescence quenching, that is, a NOR logic gate is performed.

XNOR is active only if both or neither of two inputs are present. XNOR can be operated by the situation only where both of two inputs or neither of two inputs is computed. With combined inputs of $Cu(ClO_4)_2$ in CF_3COOH and $Na_2S_2O_3$, the fluorescence emission is present at 445 nm as output 1, not only when both $Cu(ClO_4)_2$ in CF_3COOH and $Na_2S_2O_3$ are simultaneously added, but also when neither of the two inputs are added. To the solution of 2-MT^{2+}, however, if one of two (either $Cu(ClO_4)_2$ in CF_3COOH or $Na_2S_2O_3$) is added, the fluorescence emission is extinguished (threshold as 0.16), which is due to the chelation of Cu^{2+} or reduction of 2-MT^{2+} by $Na_2S_2O_3$ to 2-MT$^{\bullet +}$, as mentioned previously it is non-fluorescent. The logic circuit incorporating truth table (Fig. 9) constitutes the XNOR logic gate.

It is interesting to note that so many logic functions can be performed in a single TTF-based system with various initial states, fluorescent or non-fluorescent, under different chemical inputs. The reversible redox property of MTs affords the present system the advantage of being reversibly and selectively reset with chemical or electrochemical redox processes. The disadvantage exists with the metal ions used. The presence of 100 equiv. Fe^{2+} affects the fluorescent emission slightly,



The truth table for XNOR gate for 2-MT

$Cu^{2+}+H^+$	$Na_2S_2O_3$	PL
0	0	1 (1.00)
1	0	0 (0.16)
0	1	0 (0.15)
1	1	1 (0.70)

Fig. 9 Fluorescence emission spectra for 5.0×10^{-5} M 2-MT^{2+} in CH_2Cl_2 under different input conditions (1.0×10^{-3} M $Cu(ClO_4)_2$, 1.3×10^{-3} M CF_3COOH and 1.6×10^{-3} M $Na_2S_2O_3$) and the truth table for XNOR logic gate. The normalized fluorescence intensities (PL) are shown in the brackets.

indicating that the logic functions could be carried out with a sufficient signal–noise ratio after at least a recycle (see Fig. S12 in ESI†). The attempts to solve the precipitation with Cu^{2+} accumulated in the cycles are underway.

Conclusions

The new redox-fluorescence dependent molecules MTs were synthesized with TTF and (5-methoxy-1,3-thiazol-2-yl)pyridine unit coupled directly and rigidly. The obtained results indicate that MTs can exist in three forms—dication, cation and neutral—and they have distinct emission and absorption properties. The fluorescence emission intensity of the redox-fluorescence dependent molecule MTs can be reversibly turned depending on the oxidation state of the TTF unit, due to the peculiar property of TTF being oxidized reversibly and selectively. Based on this switchable fluorescent property, logic gate functions AND, NOT, OR, NOR, XNOR, XNAND, and INHIBIT were realized with different stable forms as an initial state. It is desirable that the molecular system is capable of changing the initial state of a molecular switch, since it can circumvent the need for an additional processor, thus providing an additional approach for molecular logic reconfiguration. Attempts to operate molecular arithmetic with this system are in progress.

Acknowledgements

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