Logic Control of the Fluorescence of a New Dyad: Spiropyran-Perylene Diimide-Spiropyran with Light, Ferric ion and Proton: Construction of a New Three-Input “AND” Logic Gate

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1. General Experimental methods
Melting points were measured with an XT_d-100X apparatus and uncorrected. \(^1\)H-NMR spectra were recorded with Bruker 300 MHz spectrometers. All chemical shifts were quoted in ppm relative to TMS. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with MALDI-TOF-MS. Elemental analysis was performed on Carlo-Erba-1106 instrument. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) Spectrophotometer in a 1-cm quartz cell. Cyclic voltammetry experiments were performed on an EGDG PAR 370 system at a scan rate of 100 mV in THF (under N\(_2\) atmosphere) using Bu\(_4\)NPF\(_6\) as electrolyte, platinum as counter and work electrodes and SCE as reference electrode. THF was dried over Na / benzophenone before use. DMF was pre-dried by standing over molecular sieves (4Å) for at least 3 days before use. All other reagents and solvents (standard grade) were used as received unless otherwise stated. THF solution of Fe(ClO\(_4\))\(_3\) was prepared for the experiments.

2. UV light and visible light irradiation experiments
The ultraviolet light irradiation experiments were performed under N\(_2\) atmosphere with a 140 W high-pressure mercury lamp at 365 nm. Similarly, the visible light irradiation experiments were performed under N\(_2\) atmosphere with a 200 W tungsten lamp (λ > 460 nm).
3. Synthetic route to dyad 1

![Synthetic route to dyad 1](images)

Scheme S1. Synthetic route to dyad 1 as well as the chemical structures of reference compounds 2 and 3.

4. Synthesis of reference compounds 2 and 3
They were prepared following the reported methods.[1,2]

Reference compound 2: yield 85%. Mp >280 °C. FTIR (KBr) 1698 and 1657 (CON). \[^1\]H NMR (300 MHz, CDCl\(_3\)): \(\delta=1.11-1.29\) (m, 6H), 1.77-1.83 (m, 6H), 1.89-1.95 (m, 4H), 2.53-2.57 (m, 4H), 5.03-5.09 (m, 2H), 7.20 (d, 4H, \(J=8.1\) Hz), 7.31 (t, 2H, \(J=8.4\) Hz), 7.48 (t, 4H, \(J=8.0\) Hz), 8.28 (s, 2H), 8.63 (d, 2H, \(J=8.4\) Hz), 9.60
(d, 2H, J = 8.4 Hz). MS (MALDI-TOF): m/z = 737.6. Elemental analysis: calculated [%] for C₄₈H₃₈N₂O₆: C 78.03, H 5.18, N, 3.79; found: C 77.92, H 5.08, N 3.60.

**Reference compound 3:** yield 77 %. M.p. 149-150 °C. FTIR ν (KBr, cm⁻¹) 2957 (alkyl-H), 1482 and 1336 (NO₂). ¹H NMR (300 MHz, CDCl₃): δ=1.21 (s, 3H), 1.29 (s, 3H), 2.71 (s, 3H), 3.82 (s, 3H), 5.88 (d, 1H, J = 10.0 Hz), 6.48 (d, 1H, J = 10.0 Hz), 6.74-6.80 (m, 3H), 6.94 (d, 1H, J = 10.1 Hz), 7.88-8.10 (m, 2H). MS (MALDI-TOF): m/z = 352.2. Elemental analysis: calculated [%] for C₂₀H₂₀N₂O₄: H 5.72, C 68.17, N 7.95; found: H 5.55, C 68.20, N 7.80.

**References**


5. **The Cyclic voltammograms of 1, 2 and 3.**

![Figure S1: The Cyclic voltammograms of 1 (solid), 2 (dash) and 3 (dot) in THF (under N₂ atmosphere) using Bu₄NPF₆ as electrolyte, platinum as counter and work electrodes and SCE as reference electrode.](image-url)
6. Absorption and fluorescence spectra of dyad 1 under different conditions
    (these are complementary to the spectra described in the manuscript)

**Figure S2.** The absorption spectra of dyad 1 (2.0×10^{-5} M, THF, 25^0C) (a) and after treatment with ultraviolet light and CF_3COOH (2.5×10^{-3} M) (b), only after addition of Fe(ClO_4)_3 (4.5×10^{-4} M) (c).

**Figure S3.** Fluorescence spectra of dyad 1 in THF (2.0×10^{-5} M, 25^0C) excited at
480 nm under the different conditions.

**Figure S4.** The absorption spectra of 3 (1.0×10⁻⁴ M, THF, 25°C) (a) before and (b) immediately after addition of 2 equiv. of Fe(ClO₄)₃.

7. **Evidences for the formation of Me·Fe⁢³⁺ complex**

After the solution of dyad 1 was treated by UV light and ferric ion, the absorption due to the ME form in the wavelength range of 590-650 nm disappeared, and a new absorption emerged in the range of 400-460 nm (see curve c of Fig. 1 of the manuscript). This new absorption may be due to the Fe³⁺ complex with ME-PI-ME (SP). Control experiments provided evidences for this assumption:

(1) UV light irradiation of the solution of reference compound 3 (see Scheme 1 in the manuscript) induced the formation of ME with the appearance of its characteristic absorption band with λₘₐₓ = 580 nm (curve b in Fig. S4). Further addition of 2 equiv. of Fe(ClO₄)₃ to the solution led to a strong absorption band with λₘₐₓ = 424 nm with the complete disappearance of the characteristic absorption band at 580 nm of ME (curve c in Fig. S4). As reported by Buncel et al (see reference 8b and 8c in the manuscript), the absorption of ME form was blue-shifted after coordination with metal ions. Thus, this new absorption band was probably due to the formation of Me·Fe³⁺ complex. Addition of K₃Fe(CN)₆ to the above solution of 3 did not lead to the formation of dark-blue precipitate, indicating there was no ferrous ion in the solution.

(2) Addition of ferrous ion to the solution of ME form also led to the hypsochromic
shift of ME form. But, only a weak absorption around 420 nm was detected.

(3) The IR spectrum of ME solution was measured: 1605.9 cm\(^{-1}\) (m), 1573.6 cm\(^{-1}\) (s), 1510.1 cm\(^{-1}\) (s), 1482.8 cm\(^{-1}\) (s), 1332.8 cm\(^{-1}\) (s), 1271.1 cm\(^{-1}\) (s), 1087.1 cm\(^{-1}\) (s). After addition of 2 equiv. of Fe(ClO\(_4\))\(_3\) to the solution of ME form, most of the absorption bands became weak: 1605.2 cm\(^{-1}\) (w), 1510.2 cm\(^{-1}\) (w), 1334.1 cm\(^{-1}\) (w), 1269.2 cm\(^{-1}\) (w), 1091.4 cm\(^{-1}\) (s), 949.2 cm\(^{-1}\) (w).

Further experimental and theoretical investigations are underway to elucidate the chemical structure of Me·Fe\(^{3+}\) complex.

**Figure S5.** The absorption spectra of 3 (1.0 \times 10^{-4} M, THF, 25°C) before (a) and after irradiation with ultraviolet light (b) and upon addition of 2 equiv. of Fe(ClO\(_4\))\(_3\) immediately after irradiation with ultraviolet light (c).