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Application and recognition behaviors of TPA-cored probes with subtle structural change

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HIGHLIGHTS

- Two novel TPA-based probes (**L1**, **L2**) were synthesized and fully characterized.
- Probe **L1** exhibited high sensitivity and selectivity for Cu^{2+}.
- Probe **L2** could respond to Cu^{2+} and Hg^{2+} in a short time.
- After mixing with Cu^{2+}, **L1** and **L2** showed great potential application in bioimaging.

GRAPHICAL ABSTRACT

The recognition abilities of two new triphenylamine(TPA)-cored probes (**L1**, **L2**) were evaluated by a series of metal ions, which showed that **L1** could recognize Cu^{2+} over other metal ions. **L2** could respond to Cu^{2+}, Hg^{2+} in a short time, but there was a slight interference between each other. Meanwhile, **L1** and **L2** (or their copper complexes) showed potential application in bioimaging.
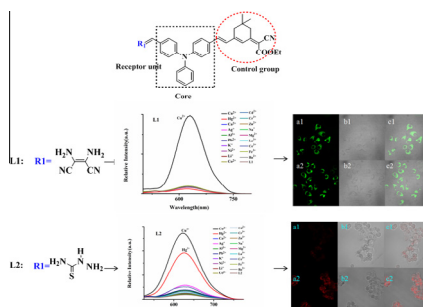
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ABSTRACT

Two new triphenylamine-cored probes (**L1**, **L2**) with different receptor units have been synthesized and fully characterized by IR, NMR and MS spectra. Their photophysical properties have been investigated in detail. The recognition abilities of two probes were evaluated by a series of metal ions, which showed that **L1** could recognize Cu^{2+} over other metal ions. **L2** could respond to Cu^{2+}, Hg^{2+} in a short time, which interferes with a little each other. The Job's plot and ^1H NMR titration of **L1** with Cu^{2+} and **L2** with Cu^{2+} (Hg^{2+}) in CD_3CN verified the coordination mode of complexes **L1**-Cu^{2+}, **L2**-Cu^{2+} and **L2**-Hg^{2+}, respectively. The limit of detection of **L2** for Cu^{2+} was lower than that of **L1** towards Cu^{2+}. The results demonstrated that the receptor units in the probes had remarkable effect on recognizing metal ions. Meanwhile, **L1** and **L2** showed potential application in bio-imaging after mixing with Cu^{2+}.

1. Introduction

Fluorescence sensing for metal ions is an attractive and important subject in supramolecular, environmental and biological chemistry [1]. An effective fluorescent chemosensor often has long emission wavelength, high sensitivity and selectivity. Long

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emission wavelength increases the detection sensitivity of fluorescent chemosensors through background signal elimination and provides the opportunity for *in vivo* diagnosis deep tissue penetration. Therefore, designing and synthesizing a fluorescence probe that owned long emission wavelength is an important direction in ion recognition domain.

Copper (Cu) is the third most abundant transition metal in the human body and plays an important role in various biological processes by being present as a cofactor of many metalloenzymes [2–5]. Therefore, the recognition of copper by several synthetic receptors is an emerging area of recent research. Mercury (Hg) is toxic metal to living body, which is associated with chemical substances: metallic mercury, inorganic and organic mercury. Among them, inorganic mercury such as mercuric sulfide, mercuric chloride and mercuric nitrate can easily pass through the skin, respiratory, and gastrointestinal tissues, which leads to DNA damage, mitosis impairment, and permanent damage to the central nervous system [6]. So the mercury (II) ion (Hg^{2+}) is one of the most dangerous and ubiquitous pollutants, which raises serious environmental and health concerns [7]. Thus, it is critical to detect trace amounts of Cu^{2+} and Hg^{2+} samples in the environment. Many reported probes [8,9] are available along with synthetic difficulties and the phenomenon of "turn-off", up to now, synthesis of the "turn-on" probes for Cu^{2+} and Hg^{2+} ions are novelty and rarely.

In this paper, we selected triphenylamine (TPA) as an electron donor because of its propeller molecular configuration as well as excellent electron donating capability [10–13] and isophorone derivatives as electron acceptor to form the D–π–A structure [14–16], which could be expected to possess longer emission wavelength and more excellent photo-physical properties. Meanwhile, we introduced the thiosemicarbazide [17] and diaminomaleonitrile [18] groups to the previous D–π–A structure, forming two A–π–D–π–A model compounds (**L1** and **L2**), which were desired to expand their recognition ability to different metal ions. Their photophysical properties, recognition ability and application in bio-imaging had been systematically investigated in this paper (Schemes 1 and 2).

2. Experimental section

2.1. Materials and instruments

Materials: diaminomaleonitrile, thiosemicarbazide, triphenylamine dialdehyde, isophorone, cyano-acetic acid ethyl ester, were available commercially. Dimethyl sulfoxide and acetonitrile were chromatographically grade. Metal salts $Cu(NO_3)_2 \cdot 3H_2O$, $Hg(OAc)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $AgNO_3$, $Al(NO_3)_3 \cdot 9H_2O$, $Pb(NO_3)_2$, KNO_3, $Ni(NO_3)_2 \cdot 6H_2O$, $LiNO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $NaNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ba(NO_3)_2$ were purchased from Aldrich and used as received.

Instruments: ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance 400 or 600 MHz NMR spectrometer using DMSO-d_6,

CD_2Cl_2, $CDCl_3$ or CD_3CN as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). The mass spectra were measured with a LTQ Orbitrap XL and AXIMA-CFR plus MALDI-TOF MS. FT-IR spectra were recorded with a Nicolet 380 spectrometer (KBr discs) in the 4000–400 cm^{-1} region and the wavenumber resolution was 4 cm^{-1}.

The Linear absorption spectra were recorded on the UV-265 spectrophotometer. The single photon excited fluorescence (SPEF) spectra measurements were performed using the Hitachi F-7000 fluorescence spectrophotometer. The concentration of sample solution was 1.0×10^{-5} mol/L. The quartz cuvettes used were of 1 cm path length. In the measurements of emission and excitation spectra, the pass width is 10 nm for **L1** and 20 nm for **L2**. Voltage: 400 V/500 V.

2.2. Synthetic method

2.2.1. Synthesis of M

4,4′-Diformyltriphenylamine [19] (6.00 g, 19.80 mmol), ethyl-2-cyano-2-(3,5,5-trimethyl-2-cyclohexeny-liden)-acetate (3.00 g, 19.80 mmol) [20] and 0.5 mL piperidine were added to 100 mL dry acetonitrile under an inert atmosphere. After stirred at 45 °C for 8 h, the resulting pomegranate mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate = 25:1 as eluent) to give 4.02 g dark red powder. Yield: 39.42%. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.81 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 6.8 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.31 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.16 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 4.27–4.17 (m, 2H), 2.96–2.62 (d, 2H), 2.41 (d, *J* = 6.7 Hz, 2H), 1.27–1.22 (m, 3H), 1.00 (d, *J* = 11.1 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.12, 165.47, 162.96, 162.49, 154.39, 153.71, 147.89, 146.45, 135.82, 135.65, 131.12, 130.38, 129.48, 129.22, 128.93, 126.09, 125.28, 123.46, 117.57, 116.78, 97.57, 61.59, 44.56, 31.93, 31.51, 28.13, 14.52. MS (MALDI-TOF): *m/z* 515.587 [(M−1)⁺, calcd 515.24]. FT-IR (cm^{-1}): 2957.45 (w), 2206.62 (m), 1873.52 (w), 1711.60 (m), 1588.17 (s), 1501.77 (m), 1288.57 (m), 1227.77 (vs), 1163.83 (m), 917.89 (m), 828.75 (vs), 697.95 (w), 555.82 (w).

2.2.2. Synthesis of L1

Diaminomaleonitrile (0.16 g, 1.50 mmol) and 0.3 mL piperidine were added to 20 mL dry benzene. The reaction mixture was refluxed for 0.5 h, and then 10 mL dry methylene chloride containing **M** (0.52 g, 1.00 mmol) was added to the reaction mixture by dropwise. After refluxed for 12 h, the residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate = 5:1 as eluent) to give 0.10 g atropurpureus powder. Yield: 16.47%. ^1H NMR (400 MHz, CDCl₃, TMS): δ (ppm) 8.33 (s, 1H), 7.69 (d, *J* = 8, 2H), 7.45–7.32 (m, 4H), 7.23–7.03 (m, 8H), 6.93–6.90 (s, 2H), 5.32–5.28 (s, 1H), 4.34–4.23 (m, 2H), 2.43–2.38
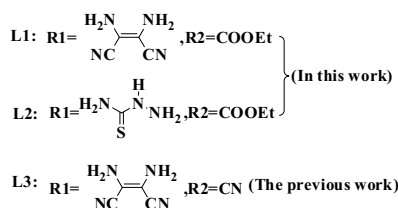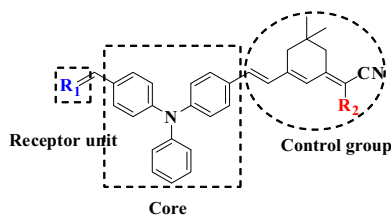
Scheme 1. Targeted molecular structure for our previous and current work.