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Di-/trinuclear cationic Ir(III) complexes: Design, synthesis and application for highly sensitive and selective detection of TNP in aqueous solution

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ABSTRACT

Novel di- and trinuclear cationic iridium(III) complexes with flexible chain functionalized triazole–pyridine moieties as bridging ligands, namely **DC-Ir** and **TC-Ir**, were successfully synthesized and their photophysical and electrochemical properties studied. Despite **DC-Ir** and **TC-Ir** have different numbers of iridium(III) cores, the almost identical emissions in both solutions and aggregation states were observed. Theoretical calculations were performed to investigate their electronic structures and rationalize the photophysical and electrochemical behaviors. Compared with the emission in the solution, they exhibit enhanced photoluminescence in the aggregation states. Benefiting from the high emission in aqueous solution, **DC-Ir** and **TC-Ir** were employed as the "turn-off" sensors to detect the explosives. The results reveal that **DC-Ir** and **TC-Ir** show fast and highly sensitive and selective detection towards 2,4,6-trinitrophenol (TNP) owing to the efficient photo-induced electron transfer as well as the strong electrostatic interaction.

1. Introduction

Solid-state luminescent materials continue to receive considerable attention due to their promising applications in optoelectronics [1], photovoltaic cells [2], bioimaging [3] and chemosensors [4–6]. More recently, the luminescent materials have been successfully utilized in the detection of explosives, which is important for homeland security and environment monitoring [7–9]. Among various detection methods, luminescence sensing utilized for the detection of explosives exhibits some advantages over other technologies, such as simplicity, high sensitivity, short response time and low cost in instrumentation [10–15]. However, the intrinsic self-quenching of luminophores caused by aggregation, namely aggregation-caused quenching (ACQ), has limitation in their practical applications [16–20]. Moreover, there remains a challenge for highly selective detecting the nitro-explosives as their similar electron affinity [21–26]. Among nitro-explosives, 2,4,6-trinitrophenol (TNP) shows the superior power compared with that of well-known 2,4,6-trinitroluene (TNT) and also widely used in many areas, however, less attention is paid to the detection of TNP [27–30]. Additionally, TNP can lead to the contamination of soil and water as its release into the environment during the commercial production and use [31,32]. Consequently, it is desirable to design and synthesize materials that can be employed to detect TNP with high selectivity and sensitivity.

Of these luminescent materials, iridium(III) complexes have emerged as promising candidates for the field of chemosensors because of their outstanding photophysical properties, including high phosphorescence quantum yields, significant Stokes shifts and relatively long excited-state lifetimes [33–36]. However, iridium(III) complexes still suffer from ACQ effect in the condensed phases as mentioned-above. Although the aggregation-induced emission (AIE) materials showing enhanced emission in the aggregated states can offer a route to overcome this problem, there are some obstacles for the design of AIE-active iridium(III) complexes as the AIE mechanism is still not clear [19,37–40]. Recently, a new strategy for mitigating ACQ effect is to design multinuclear iridium(III) complexes [41,42]. Although a lot of applications based on mononuclear iridium(III) complexes have been developed, the multinuclear iridium(III) complexes are attractive as

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their properties can be easily tuned by changing the bridging and cyclometalated ligands [43]. In addition, the present of the additional metal centres in multinuclear iridium(III) complexes may facilitate spin-orbit coupling (SOC) pathways, thus increasing the efficiencies from harvesting both singlet and triplet excitons [44,45].

To enrich the family of the multinuclear iridium(III) complexes and broaden the application in the efficient detection of explosives, herein, we present new cationic dinuclear and trinuclear iridium(III) complexes featuring 1,2-diphenyl-1*H*-benzoimidazole (Hpbi) as the cyclometalated ligand and new complexes **L1** and **L2** as bridging ligands, namely **DC-Ir** and **TC-Ir**, respectively (see Scheme 1 and Scheme 2). The ionic characters of **DC-Ir** and **TC-Ir** can facilitate the good solubility in the polar solvents, and the possibility for the detection of TNP in the aqueous media is thus feasible. Furthermore, TNP can readily dissociate in aqueous solvents, forming 2,4,6-trinitrophenolate in the mixtures. The presence of strong interactions between the cations of **DC-Ir** and **TC-Ir**, and 2,4,6-trinitrophenolate will enhance its selectivity toward TNP compared with the other explosives. As expected, the designed **DC-Ir** and **TC-Ir** possess the strong photoluminescence in the aggregation states, and both complexes also exhibit high selectivity and sensitivity for the detection of TNP in aqueous media.

2. Experimental

2.1. General information

^{1}H NMR and ^{19}F NMR spectra were recorded using a Bruker AV 500 MHz or 600 MHz with tetramethylsilane (TMS) as the internal standard. The molecular weights of complexes were tested by using matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry. UV–vis absorption spectra were recorded on Cary 500 UV-vis-NIR spectrometer. Emission spectra were recorded using the F-4600 FL spectrophotometer. The excited-state lifetime was measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photon counting technique. The photoluminescence quantum yields (PLQYs) were determined using an integrating sphere system. Transmission electron microscopy (TEM) of the sample was performed using a TECNAI F20 microscope. The samples were prepared by placing microdrops of the colloid solution on a holey carbon copper grid. All materials and solvents from commercial suppliers were used without further purification.

2.2. Synthesis

The intermediates **1a**, **2a**, **1b** and **2b** were synthesized according to the literature procedures [46].

2.2.1. Synthesis of 3-methoxy-9-(4-(3-phenyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)-butyl)-9H-carbazole (*1c*)

3-methoxy-9*H*-carbazole (**1b**, 0.16 g, 0.81 mmol), 2-(1-(4-bromobutyl)-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (0.30 g, 0.84 mmol) were dissolved in toluene (15 mL), then tetrabutyl ammonium bromide (TBAB, 0.20 g, 0.62 mmol) and 50% NaOH aqueous solution (5 mL) were added in the mixture. The mixture was filled with nitrogen and heated at 60 °C. Then the reaction was stopped after 6 h. After cooling to ambient temperature, the mixture was extracted with dichloromethane. The organic layer was washed with saturated salt water several times and dried with Na_2SO_4. Then the organic solvent was removed by rotary evaporator. Using the petroleum ether/ethyl acetate (10:3, in volume) as the eluent, the crude product was purified by column chromatography. The white pure solid was obtained with a higher yield. (75%).^{1}H NMR (500 MHz, d_6-DMSO, ppm):δ 8.64–8.65 (m, 1H), 8.21 (d, J = 7.5 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.00–8.05 (m, 3H), 7.68 (d, J = 2.0 Hz, 1H), 7.44–7.54 (m, 6H), 7.32–7.35 (m, 1H), 7.10–7.13 (m, 1H), 6.98–7.00 (m, 1H), 4.83 (t, J = 7.0 Hz, 2H), 4.39 (t, J = 7.0 Hz, 2H), 3.83 (s, 3H), 1.91–1.95 (m, 2H), 1.78–1.82 (m, 2H).

2.2.2. Synthesis of 3,6-dimethoxy-9-(4-(3-phenyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)-butyl)-9H-carbazole (*2c*)

The synthesis of **2c** was similar to that of **1c** except that the precursor **1b** was replaced by 3,6-dimethoxy-9*H*-carbazole (**2b**). Using the petroleum ether/ethyl acetate (10:3, in volume) as the eluent, the crude product was purified by column chromatography. The white pure solid was obtained with a higher yield. (72%).^{1}HNMR (500 MHz, d_6-DMSO, ppm):δ 8.65 (d, J = 4.5 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.00–8.05 (m,3H), 7.68 (d, J = 2.5 Hz, 2H), 7.45–7.53 (m,4H), 7.40 (d, J = 9.0 Hz, 2H), 6.94–6.96 (m,2H), 4.81 (t, J = 7.0 Hz, 2H), 4.33(t, J = 7.0 Hz, 2H), 3.84 (s,3H), 1.90 (t, J = 7.5 Hz, 2H), 1.75 (t, J = 7.0 Hz, 2H).

2.2.3. Synthesis of 9-(4-(3-phenyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)-butyl)-9H-carbazol-3-ol (*1d*)

The intermediate **1c** (0.20 g, 0.42 mmol) was dissolved in dry CH_2Cl_2 (25 mL), then the mixture was cooled to 0 °C. The solution of BBr_3in dry CH_2Cl_2 (0.16 mL 1 M solution in CH_2Cl_2, 1.69 mmol) was added drop wise into the mixture. Then the reaction was stopped after 4 h at 0 °C. After the mixture was carefully quenched with methanol, the saturated solution of $NaHCO_3$ was added. The mixture was extracted with dichloromethane and washed with saturated salt water. The solvent was removed by rotary evaporator after dried with Na_2SO_4. Using the petroleum ether/dichloromethane (2:1, in volume) as the eluent, the crude product was purified by column chromatography. The white pure solid was obtained with a higher yield. (82%). ^{1}H NMR (500 MHz, d_6-DMSO, ppm):δ 8.97 (s, 1H), 8.65-8.66 (m, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.98–8.06 (m,4H), 7.43–7.54 (m, 6H), 7.35 (d, J = 8.5 Hz, 1H), 7.28–7.32 (m, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.87–6.89 (m, 1H), 4.84 (t, J = 7.0 Hz, 2H), 4.05–4.36 (m, 2H), 1.92–1.96 (m, 2H), 1.77–1.82 (m, 2H).

2.2.4. Synthesis of 9-(4-(3-phenyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-yl)butyl)-9H-carbazole-3,6-diol (*2d*)

The synthesis of **2d** was similar to that of **1d** except that the precursor **1c** was replaced by **2c**. Using the petroleum ether/methanol-ethyl/acetate (10:3:2, in volume) as the eluent, the crude product was purified by column chromatography. The red solid was obtained. Due to poor solubility, the intermediate **2d** was used without purification.

2.2.5. Synthesis of ancillary ligand L1

9-(4-(3-phenyl-5-(pyridin-2-yl)-1*H*-1,2,4-triazol-1-yl)-butyl)-9*H*carbazol-3-ol (**1d**, 0.60 g, 1.30 mmol), 2-(1-(4-bromobutyl)-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (0.51 g, 1.44 mmol) were dissolved in toluene (50 mL), then TBAB (0.50 g, 1.55 mmol) and 50% NaOH aqueous solution (10 mL) were added in the mixture. The mixture was filled with nitrogen and heated at 60 °C. Then the reaction was stopped after 10 h. After cooling to ambient temperature, the mixture was extracted with dichloromethane. The organic layer was washed with saturated salt water several times and dried with Na_2SO_4. Then the organic solvent was removed by rotary evaporator. Using the petroleum ether/ethyl acetate (2:1, in volume) as the eluent, the crude product was purified by column chromatography. The white pure solid was obtained with a higher yield. (79%). ^{1}H NMR (500 MHz, d_6-DMSO,