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Photo-physical properties of donor-acceptor-radical triad based on functionalized tetrathiafulvalene and nitronyl nitroxide radical

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ABSTRACT

An acceptor-donor-radical triad based on tetrathiafulvalene (TTF)-fused (benzimidazol-2-yl)-pyridine (bzip) which is alkylated with a nitronyl nitroxide (NIT) radical derivative, has been designed and synthetized. Its X-ray structure has been refined showing a complex arrangement of head-to-tail dimers of the TTF-bzip moieties and a 1D network of short contacts between the NIT radicals. Its electrochemical behavior has been studied by cyclic voltammetry (CV) showing that the TTF and NIT moieties can be reversibly and independently oxidized. The occurrence of intramolecular ligand charge transfers (ILCT) of both TTF → bzip and TTF → NIT nature has been evidenced by UV–visible electronic absorption spectroscopy coupled to TD-DFT calculations. Moreover, these calculations and RPE measurements confirmed the radical form ($S = ½$) of the compound as well as the spin density mainly localized on the methyl-benzo-[1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl] unit. Both emissions of the NIT radical and TTF-based molecular skeleton have been observed with a tunable intensity ratio depending on the irradiation energy. Finally, this new triad may be a valuable candidate for the construction of multi-property compounds by coordination of metallic ions either on the TTF-based molecular skeleton or on the NIT moieties.

1. Introduction

Chemists and physicists have been working hand-in-hand for more than two decades in order to design multifunctional materials with controllable physicochemical properties. In particular, they have tried to conceive molecular architectures able to force interactions between these properties until reaching a synergetic effect between them. Multiferroism and magneto-chiral dichroism are maybe the most representative examples of synergy between several different physical properties [1-3]. In this line, this work is focused on the search of molecular compounds that exhibit both electronic conductivity and magnetic behavior. To obtain such compounds, we used the extremely rich chemistry based on the tetrathiafulvalene (TTF) core in order to take advantage of its redox activity and potential electronic conductivity [4]. It has been demonstrated that a fruitful strategy is to add to the TTF core localized electrons thanks to transition metals (3*d* and 4*d*) [5-10] or lanthanides [11-12]. Such π-*d* and π-*f* systems have shown exciting transport properties such as antiferromagnetic-superconductor or magnetic-field induced superconducting transition [13-14] but also have given rise to redox-active [15-18], or luminescent single-molecule magnets (SMM) [19-20]. The successes in obtaining such multi-property molecular systems were guaranteed thanks to two approaches that allow the observation of interactions between mobile electrons of the organic network and localized electrons of the paramagnetic metals: i) through-space interactions or ii) covalent bonds. Whereas the first strategy leads to very weak π-*d*/π-*f* interactions, the second one might enhance them. The “through-space” approach is commonly used thanks to a plethora of functionalization of the TTF core with organic moieties suitable to coordinate metal ions (amino, nitrile, phenolate, phosphino, β-

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diketonate, pyrazine, pyrimidine, pyridine, pyridine-*N*-oxide, bipyridine…) [5], [21], [22]. All of these organic coordinating groups are magnetically innocent (S = 0). However, an underdeveloped strategy consists in the functionalization of the TTF core with a stable organic radical (S = ½) to play the magnetic relay between the π mobile electrons and the paramagnetic metal. The design and elaboration of such "TTF-radical" dyads are very challenging and to date only few researchers took this synthetic route: Sugawata et al. [23-26] developed the functionalization of the TTF core with nitrosyl or nitronyl nitroxide spin carriers while Yamaguchi et al. [27] and Datta et al. [28], [29], studied such donor-radical dyads from a computational point of view. Additionally, Pilkington et al. [30], [31], used the verdazyl moiety as stable radical while Veciana et al. exploited the perchlorotriphenylmethyl radicals [32-36] to design their dyads.

In our group, a family of donor-acceptor dyads based on the 2-(4,5-(4,5-bis(propylthio)-tetrathiafulvalenyl)-1*H*-benzimidazol-2-yl)-pyridine molecular skeleton **1** [37], [38], has been previously designed and alkylated with various organic moieties such as 2-pyridyl [39], dimethyl-2,2'-bipyridyl [40], di-(pyrazol-1-yl)-4-pyridyl [40] and 4-pyridyl-*N*-oxide [41]. In the present work, following this synthetic strategy, **1** has been alkylated with the 4-bromomethylbenzo(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) organic radical **2** and leads to the formation of the 2-{1-[methylbenzo(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazoline)]-4,5-[4,5-bis(propylthio)-tetrathiafulvalenyl]-1*H*-benzimidazol-2-yl}pyridine acceptor-donor-radical triad **3**. In the next lines, X-ray structures of **2** and **3** are analyzed as well as the electrochemical, photo-physical and magnetic properties of **3**.

2. Experimental section

2.1. General

The ligand 2-(4,5-(4,5-bis(propylthio)-tetrathiafulvalenyl)-1*H*-benzimidazol-2-yl)-pyridine [38] **1** and the organic radical precursor 4-bromo-methylbenzo(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) **2** [42-44] were synthesized following previously reported methods. The 4-(bromomethyl)benzaldehyde was purchased from Acros company while all other reagents were purchased from Aldrich Co., Ltd. and used without further purification.

2.2. Synthesis

4-bromomethylbenzo(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) (2). Slow evaporation of a CH_2Cl_2/*n*-hexane mixture affords single-crystal suitable for X-ray diffraction studies.

2-{1-[methylbenzo(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazoline)]-4,5-[4,5-bis(propylthio)-tetrathiafulvalenyl]-1*H*-benzimidazol-2-yl}pyridine (3). 2-(4,5-(4,5-bis(propylthio)-tetrathiafulvalenyl)-1*H*-benzimidazol-2-yl)-pyridine **1** (33.3 mg, 0.06 mmol) and K_2CO_3 (13.3 mg, 0.10 mmol, 1.5 equiv) were added to anhydrous DMF (3 mL), and then the mixture was stirred for 30 min under argon. A solution of anhydrous DMF (2 mL) containing 4-bromo-methyl-benzo-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) **2** (15 mg, 0.046 mmol, 0.8 equiv) was added, and the resulting mixture was stirred for 2 h at room temperature. Then additional K_2CO_3 (13.3 mg, 0.10 mmol, 1.5 equiv) and of 4-bromo-methyl-benzo-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) (1) (10 mg, 0.03 mmol, 0.5 equiv) were added. The mixture was stirred at room temperature overnight under argon atmosphere.

The solvents were eliminated under vacuum and the residue was dissolved in CH_2Cl_2, filtered, concentrated to 5 mL and finally *n*-hexane (5 mL) was added. Slow evaporation in the dark gave green single crystals of **3** suitable for X-ray study. Yield: 37 mg (75%). Anal. Calcd (%) for $C_{36}H_{38}N_5O_2S_6$: C 56.47, H 4.97, N 9.15; found: C 56.55, H 5.01, N 9.09. I.R. (KBr): 2959, 2926, 2866, 2853, 1632, 1586, 1565, 1443, 1423, 1387, 1364, 1320, 1220, 1162, 1103, 851, 786, 738, 701, 613 and 540 cm^{-1}.

2.3. Crystallography

Single crystals of **2** and **3** were mounted on a D8 VENTURE Bruker-AXS diffractometer for data collection (MoK$_\alpha$ radiation source, $\lambda = 0.71073$ Å), from the Centre de Diffractométrie (CDIFX), Université de Rennes 1, France. Structures were solved with a direct method using the SHELXT program [45] and refined with a full matrix least-squares method on F^2 using the SHELXL-14/7 program [46]. Crystallographic data are summarized in Table 1. Complete crystal structure results as a CIF file including bond lengths, angles, and atomic coordinates are deposited as Supporting Information.

2.4. Physical measurements

The elementary analyses of the compounds were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Cyclic voltammetry was carried out in CH_2Cl_2 solution, containing 0.1 M of $N(C_4H_9)_4PF_6$ as supporting electrolyte. Voltammograms were recorded at 100 mV s^{-1} at a platinum disk electrode. The potentials were measured *versus* a saturated calomel electrode (SCE). Absorption spectra were recorded on a Varian Cary 5000 UV–Visible–NIR spectrometer equipped with an integration sphere. The solid and solution emission and excitation spectra were measured using a Horiba-Jobin Yvon Fluorolog-3® spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at a 90° angle for diluted solution and for solid state measurements by a red-sensitive Hamamatsu R928 photomultiplier tube (sensitivity 190–860 nm). Spectra were reference corrected for both the

Table 1
X-ray crystallographic data for **2** and **3**.

Compounds	**2**	**3**
	CCDC 1535280	CCDC 1535281
Formula	$C_{14}H_{18}BrN_2O_2$	$C_{72}H_{76}N_{10}O_4S_{12}$
M/g.mol^{-1}	326.2	1530.14
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c* (N°15)	*P*-1 (N°2)
Cell parameters	$a = 23.8847(12)$ Å	$a = 13.6015(14)$ Å
	$b = 10.6482(6)$ Å	$b = 16.2250(20)$ Å
	$c = 11.7735(6)$ Å	$c = 17.6720(20)$ Å
	$\beta = 95.459(2)°$	$\alpha = 68.538(4)°$
		$\beta = 84.066(4)°$
		$\gamma = 88.706(4)°$
Volume/Å^3	2980.8(3)	3609.6(7)
Z	8	2
T/K	150(2)	150(2)
2θ range/°	$5.34 \le 2\theta \le 55.04$	$5.76 \le 2\theta \le 55.96$
ρ_{calc}/g.cm^{-3}	1.454	1.408
μ/mm^{-1}	2.758	0.420
Number of reflections	3411	77927
Independent reflections	2655	16508
R_{int}	0.0523	0.0757
$Fo^2 > 2\sigma(Fo)^2$	1336	10449
Number of variables	172	883
R_1, wR_2	0.0387, 0.1043	0.0729, 0.1796