Supplementary Material

Spectroscopic recognition of metal ions and non-linear optical (NLO) properties of some fluorinated poly(1,3,4-oxadiazole-ether)s

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- *1H NMR data*

Also, its molecular structure were established using ^1H NMR data (chloroform-d, 400 MHz, ppm) such as: for **BisFOx** sample, 8.10 (4H, d), 7.63 (1H, d), 7.50 (1H, t), 7.43 (2H, d), 7.18 (4H, d), 7.15 (4H, d), 7.05 (4H, d); for **6FOx** sample, 8.12 (4H, d), 7.42 (4H, d), 7.20 (4H, d), 7.06 (4H, d) and for **9FOx** sample, 7.09 (4H, d, 8.6 Hz, H-2), 7.14 (4H, d, 8.7 Hz, H-3), 7.18 (4H, d, 8.3 Hz, H-13), 7.67 (2H, bs, H-8), 7.91 (1H, bs, H-10), 8.13 (4H, d, 8.2 Hz, H-14) [1].
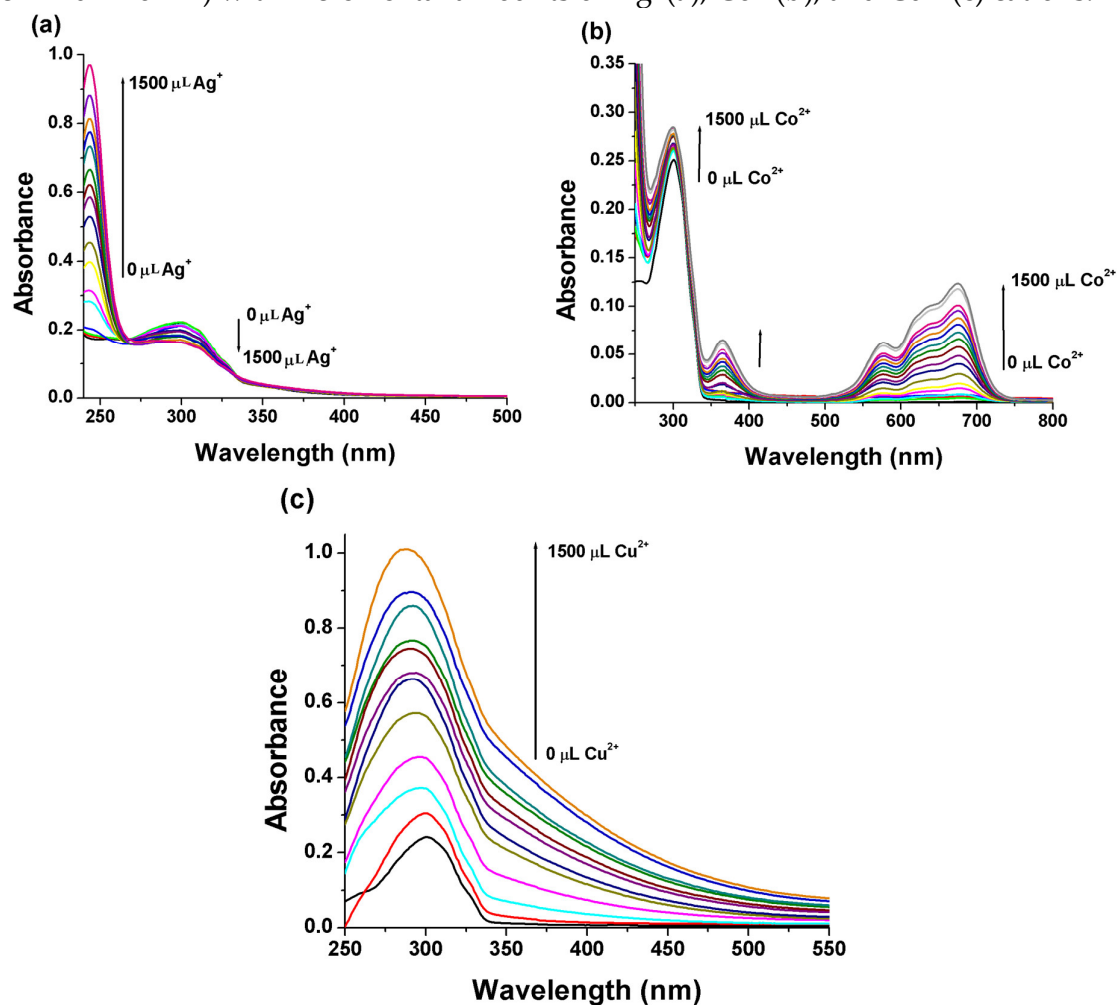
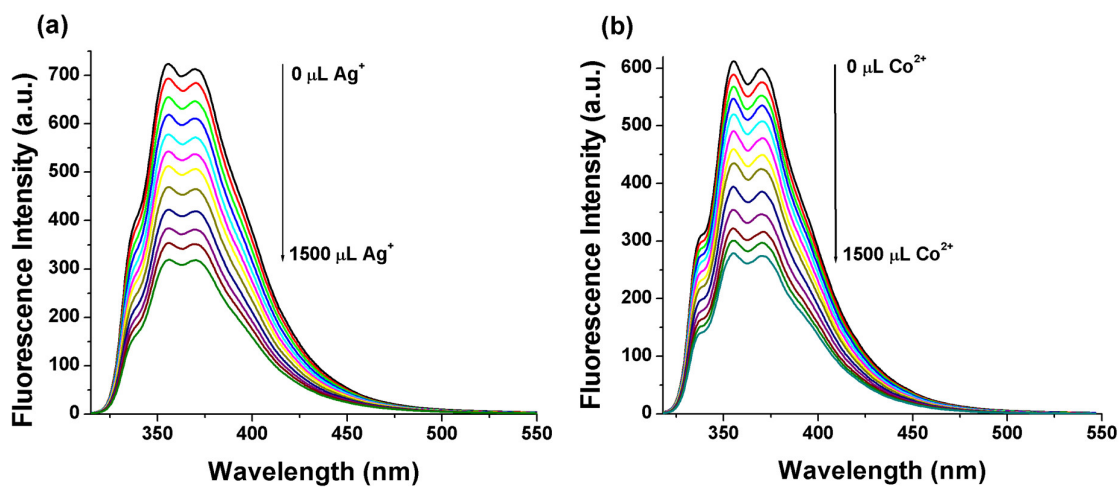- *Changes in absorption and fluorescence spectra after addition of metal ions*
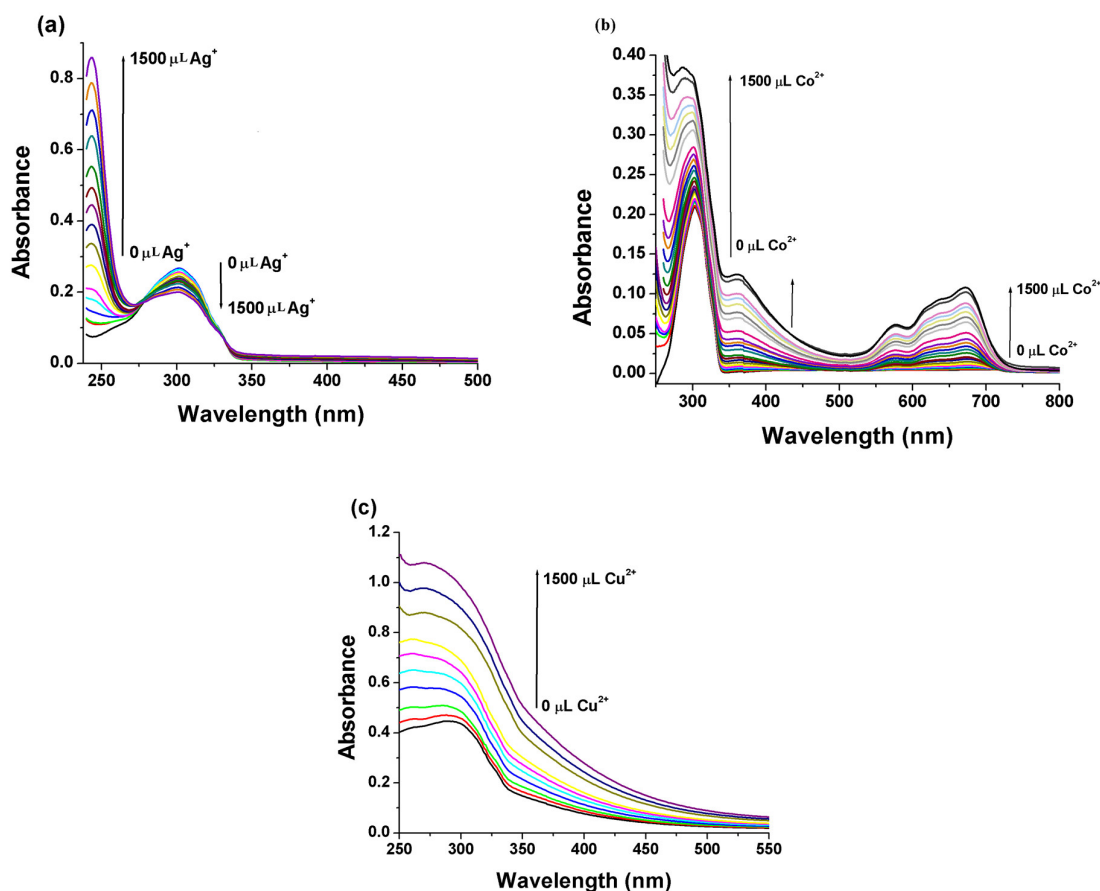
Figure S1. Absorption spectral changes during the titration of the **9FOx** sample ($c=1\times10^{-5}$ mol L^{-1}) with incremental amounts of Ag$^+$ (**a**), Co^{2+} (**b**), and Cu^{2+} (**c**) cations.

Figure S2. Absorption spectral changes during the titration of the **6FOx** sample ($c=1\times10^{-5}$ mol L^{-1}) with incremental amounts of Ag$^+$ (**a**), Co^{2+} (**b**), and Cu^{2+} (**c**) cations.
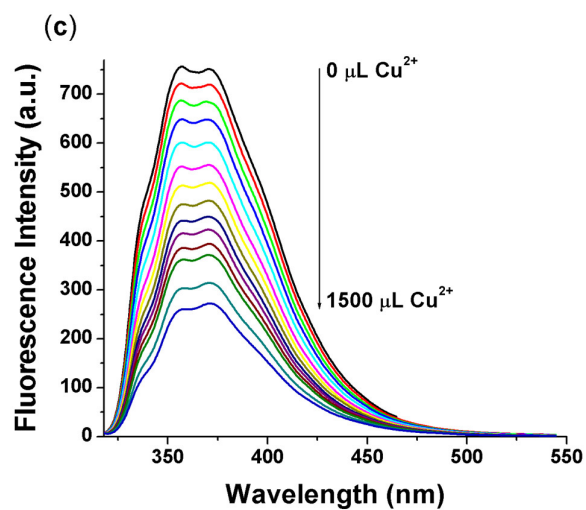
Figure S3. Fluorescence spectral changes during the titration of the **9FOx** sample (c=1x10^{-5} mol L^{-1}) with incremental amounts of Ag$^+$ (a), Co^{2+} (b), and Cu^{2+} (c) cations.
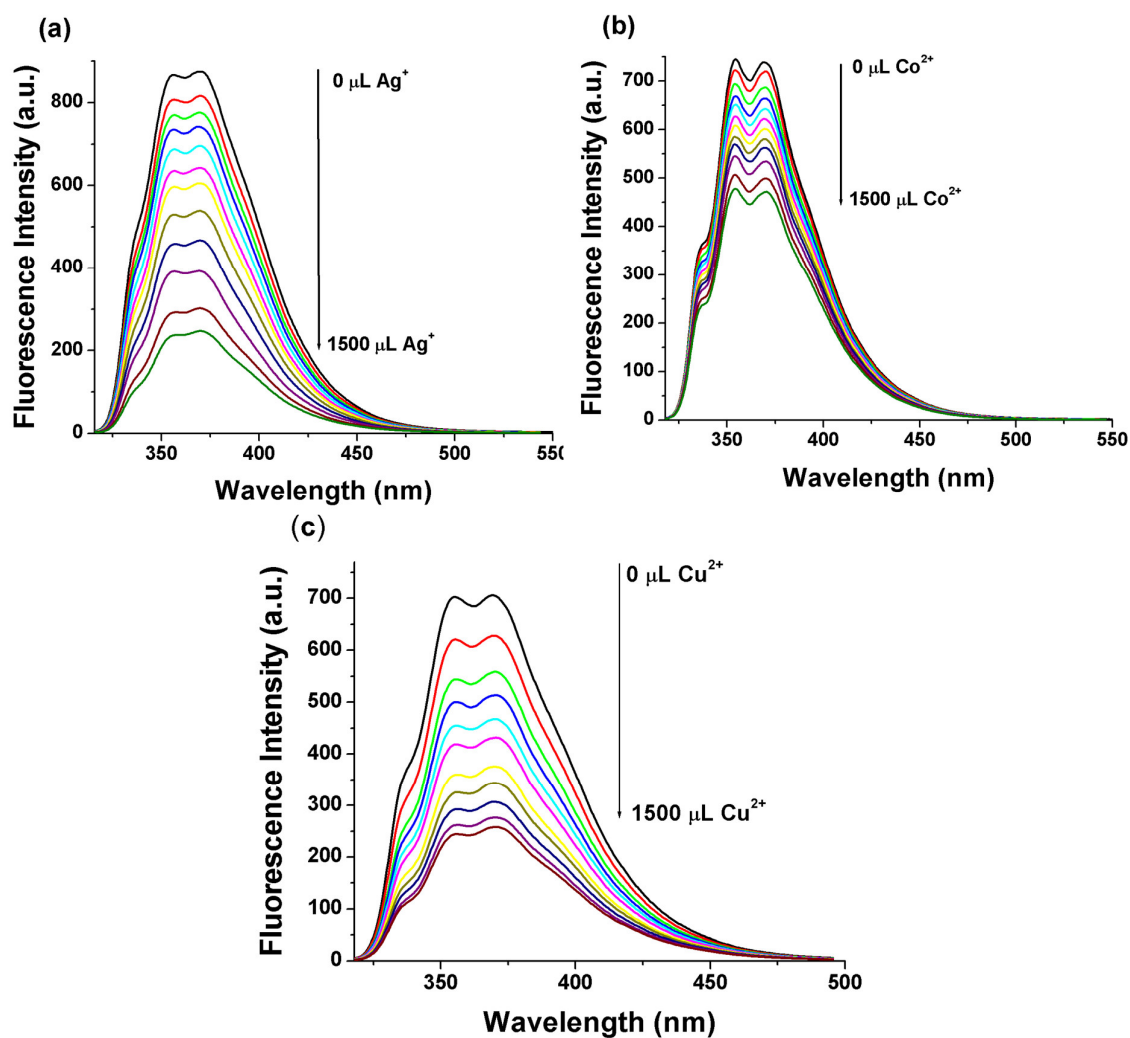
Figure S4. Fluorescence spectral changes during the titration of the **6FOx** sample ($c=1\times10^{-5}$ mol L^{-1}) with incremental amounts of Ag^+ (**a**), Co^{2+} (**b**), and Cu^{2+} (**c**) cations.

- *Determination of Onsager cavity radius (a) for BisFOx derivative*

The solvent Onsager cavity radius (a) of the **BisFOx** sample was estimated by the following equation [2]:

$$a = (3M/4\pi\rho N_A)^{1/3} \tag{S1}$$

where, M is the molar mass; N_A is Avogadro's number ($6.02214076 \times 10^{23}$) and ρ is the molecular density of **BisFOx** molecules, which was calculated using Bicerano's [3] atomic and bond incremental method, by Eq. (S2):

$$\rho(T) \equiv M / V(T) \tag{S2}$$

where M is the molecular weight of the solute and the V(T) is the molar volume, expressed as:

$$V(298K) \approx 3.642770 \cdot {}^0\chi + 9.798697 \cdot {}^0\chi^v - 8.542819 \cdot {}^1\chi + 21.693912 \cdot {}^1\chi^v + 0.978655 \cdot N_{MV} \tag{S3}$$

where

- ${}^0\chi$ and ${}^0\chi^v$ are the zero-order simple (${}^0\chi = \sum\left(1/\sqrt{\delta}\right)$) and valence (${}^0\chi^v = \sum\left(1/\sqrt{\delta^v}\right)$) connectivity indices;

- δ and δ^v are the atomic simple and valence connectivity indices;

- 1χ and ${}^0\chi^v$ are the zero-order simple (${}^1\chi = \sum\left(1/\sqrt{\beta}\right)$) and valence ($1\chi^v = \sum\left(1/\sqrt{\beta^v}\right)$) connectivity indices. The values of these parameters for C, N, and O atoms are listed in **Table S1.**

Table S1. Values of the atomic simple connectivity indices, δ , and valence connectivity indices δ^v used for calculating zero- and first-order connectivity indices [3].

Atom	Hyb	N_H	δ	δ^v
C	sp3	3	1	1
		2	2	2
		0	4	4
	sp2	1	2	3
		0	3	4
N	sp2	0	2	5

| O | sp3 | 0 | 2 | 6 |

- N_{MV} is the total values of the number of elements (carbon-carbon double bonds, nonaromatic rings and other elements from the repeating unit), calculated based on Eq. (S4).

$$N_{MV} \equiv 24N_{Si} - 18N_{(-S-)} - 5N_{sulfone} - 7N_{Cl} - 16N_{Br} + 2N_{(backbone\,ester)} + 3N_{ether} + 5N_{carbonate} +$$
$$+ 5N_{C=C} - 11N_{cyc} - 7 \cdot (N_{fused} - 1)(\text{last term only to be used if } N_{fused} \geq 2) \qquad (S4)$$

- here N_{Si}, N_{-S-}, $N_{sulfone}$, N_{Cl}, N_{Br}, is the number of silicon atoms, sulfur atoms in the lowest oxidation state, sulfur atoms in the highest oxidation state, chlorine atoms, bromine atoms, respectively in the polymeric repeat unit; $N_{(backbone\,ester)}$ is the number of ester (-COO-) groups, in the backbone of the repeat unit; N_{ether} is the total number of ether (-O-) linkages, in the polymeric repeat unit; $N_{carbonate}$ is the total number of carbonate (-OCOO-) groups, in the polymeric repeat unit; $N_{(C=C)}$ is the number of carbon-carbon double bonds, in the repeat unit; N_{cyc} is the number of nonaromatic rings with no double bonds along any of the edges of the ring; $N_{(fused-1)}$ is the rings in fused ring structures.

Thus, the values for the V(T) and ϱ parameters of **BisFox** sample are:

V(T) = 3.642770*32.89 + 9.798697 *23.545 + 8.542819*22.226 + 21.693912*18.368 + 0.978655*81 = 638.393 cc/mole   (S5)

$\varrho = (630/638.393) = 0.987$ g cm^{-3}

Replacing, the calculated ϱ values (0.987 g cm^{-3}) in **Eq. S1,** we found that the values for the Onsager cavity radius of the **BisFox** sample be 6.33 Å.

References

1. Ipate, AM.; Homocianu, M.; Hamciuc, C.; Airinei, A.; Bruma, M. Photophysical behavior of some aromatic poly1,3,4-oxadiazole-ethers derivatives. *Spectrochim. Acta A Mol. Biomol. Spectrosc* **2014,** *123*, 167–175. https://doi.org/10.1016/j.saa.2013.12.057.

2. Suppan, P. Excited-state dipole moments from absorption/fluorescence solvatochromic ratios, *Chem. Phys. Lett.* **1983,** *94,* 272–275. https://doi.org/10.1016/0009-2614(83)87086-9.

3. Bicerano, J. Prediction of Polymer Properties; Marcel Dekker: New York, NY, USA, 2000.