Electronic Supplementary Material (ESI) for RSC Advances.

Spirooxazine Molecular Switches with Nonlinear Optical Responses as Selective Cation Sensors

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Table S1. Selected NBO second-order interaction energies (E_2, kcal mol^{-1}) of the cation compounds at the B3LYP/6-31G(d)/LanL2DZ level.

Compound	Donor NBO(*i*)→Acceptor NBO(*j*)	E_2
MC*Li^+	LP1 N1→LP*1 Li	13.63
	LP2 O1→LP*1 Li	25.19
MC*Na^+	LP1 N1→LP*1 Na	7.65
	LP1 O1→LP*1 Na	9.55
MC*K^+	LP1 N1→LP*1 K	0.33
	LP1 O1→LP*1 K	5.27
MC*Mg^{2+}	LP1 N1→LP*1 Mg	37.18
	LP2O1→LP*1 Mg	37.67
MC*Ca^{2+}	LP1 N1→LP*1 Ca	9.83
	LP2O1→LP*1 Ca	11.71
MC*Fe^{2+}	LP1 N1→LP*1 Fe	69.67
	LP3 O1→LP*4 Fe	60.22
MC*Zn^{2+}	LP1 N1→LP*6 Zn	55.45
	LP2 O1→LP*6 Zn	54.51
MC*Ag^+	LP1 N1→LP*1 Ag	16.51
	LP2 O1→LP*6 Ag	24.90

LP, 1-center valence lone pair. LP*, 1-center valence antibond lone pair.

Table S2. Individual components of first hyperpolarizabilities and total first hyperpolarizabilities (10^{-30} esu), computed at various levels of theory.

Compound	Functionals	β_x	β_y	β_z	β_{tot}
SP	CAM-B3LYP	0.5	-3.9	-1.0	4.0
	BHandHLYP	1.2	-3.7	-0.7	3.9
	M06-2X	0.2	-3.6	-1.0	3.7
	ωB97XD	0.6	-3.8	-1.0	4.0
MC*Li^+	CAM-B3LYP	-50.0	-31.9	1.4	59.3
	BHandHLYP	-52.0	-31.8	1.3	60.9
	M06-2X	-50.6	-31.2	1.5	59.4
	ωB97XD	-48.6	-31.9	1.4	58.2
MC*Na^+	CAM-B3LYP	-58.2	-30.9	5.5	66.1
	BHandHLYP	-59.3	-30.4	5.3	66.9
	M06-2X	-59.7	-30.4	5.5	67.2
	ωB97XD	-57.0	-30.6	5.4	64.9
MC*K^+	CAM-B3LYP	-41.3	-31.8	3.1	52.3
	BHandHLYP	-40.9	-30.8	2.9	51.3
	M06-2X	-43.5	-31.6	3.1	53.9
	ωB97XD	-40.8	-31.3	3.1	51.5
MC*Mg^{2+}	CAM-B3LYP	-55.9	-39.5	6.5	68.7
	BHandHLYP	-63.0	-39.9	6.4	74.8
	M06-2X	-49.6	-37.1	6.5	62.3
	ωB97XD	-53.2	-40.2	6.6	67.1
MC*Ca^{2+}	CAM-B3LYP	-75.3	-33.8	18.9	84.6
	BHandHLYP	-82.4	-34.7	17.9	91.2
	M06-2X	-68.5	-31.2	18.9	77.6
	ωB97XD	-73.4	-34.2	18.1	83.0
MC*Fe^{2+}	CAM-B3LYP	-20.0	-32.8	0.3	38.4
	BHandHLYP	-31.0	-33.7	0.8	45.8
	M06-2X	-14.3	-28.0	0.9	31.5
	ωB97XD	-15.5	-33.5	0.4	36.9
MC*Zn^{2+}	CAM-B3LYP	-50.6	-41.6	6.1	65.8
	BHandHLYP	-58.1	-42.6	5.8	72.3
	M06-2X	-42.5	-38.3	6.2	57.5
	ωB97XD	-47.6	-42.4	6.2	64.0
MC*Ag^+	CAM-B3LYP	-53.4	-34.0	4.6	63.5
	BHandHLYP	-55.8	-33.4	4.4	65.2
	M06-2X	-54.8	-33.3	4.6	64.2
	ωB97XD	-52.2	-34.1	4.5	62.5

Table S3. The first hyperpolarizabilities (10^{-30} esu) of MC*Ca^{2+} calculated at the CAM-B3LYP level using various basis sets.

Basis set	β_x	β_y	β_z	β_{tot}
6-31+G(d)	-75.3	-33.8	18.9	84.6
6-31++G(d)	-75.1	-33.8	-19.0	84.5
6-31+G(d,p)	-75.0	-33.9	18.9	84.4
6-31++G(d,p)	-74.8	-33.8	18.9	84.2
6-311++G(d,p)	-76.8	-34.0	19.7	86.3

Table S4. The first hyperpolarizabilities (10^{-30} esu) of the compounds (SP, MC*K^+, MC*Ca^{2+}, MC*Fe^{2+}, and MC*Zn^{2+}) computed in gas phase and methanol solvent at various levels of theory.

Compounds	Functionals	β_{tot}	
		Gas phase	Methanol solvent
SP	CAM-B3LYP	4.0	10.4
	BHandHLYP	3.9	9.6
	M06-2X	3.7	9.8
	ωB97XD	4.0	10.3
MC*K^+	CAM-B3LYP	52.3	194.8
	BHandHLYP	51.3	185.6
	M06-2X	53.9	201.7
	ωB97XD	51.5	195.5
MC*Ca^{2+}	CAM-B3LYP	84.6	221.7
	BHandHLYP	91.2	231.0
	M06-2X	77.6	204.6
	ωB97XD	83.0	224.0
MC*Fe^{2+}	CAM-B3LYP	38.4	91.4
	BHandHLYP	45.8	82.2
	M06-2X	31.5	92.3
	ωB97XD	36.9	96.3
MC*Zn^{2+}	CAM-B3LYP	65.8	165.3
	BHandHLYP	72.3	182.1
	M06-2X	57.5	141.1
	ωB97XD	64.0	162.4