chemosensors

MDPI

Supplementary Material

Prediction of Carbonate Selectivity of PVC-Plasticized Sensor Membranes with Newly Synthesized Ionophores through QSPR Modeling

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[2] JSVC Vekton, Ul. 2-oy Luch 9, 192019 Saint-Petersburg, Russia; polukeev.valeriy@mail.ru
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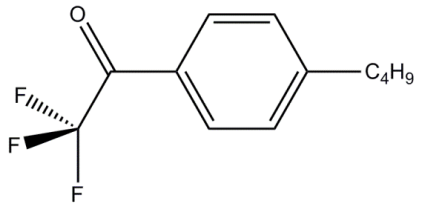
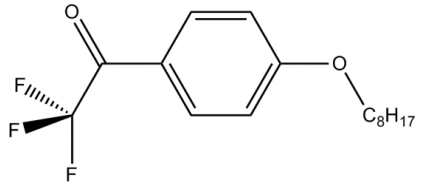
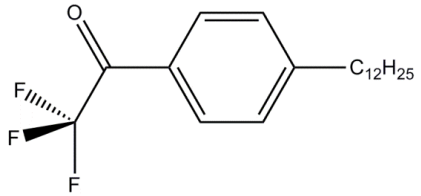
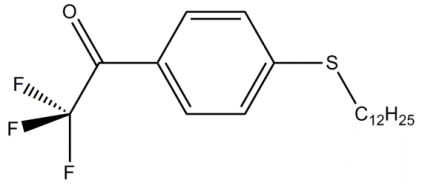
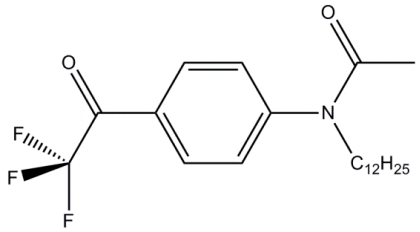
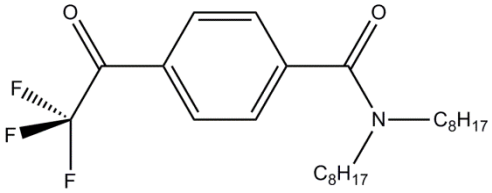
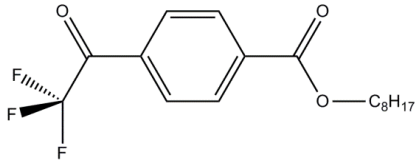
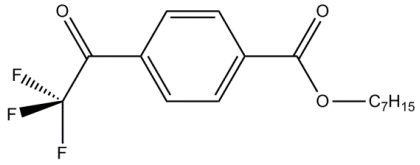
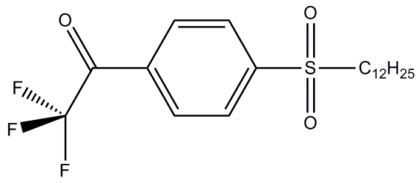
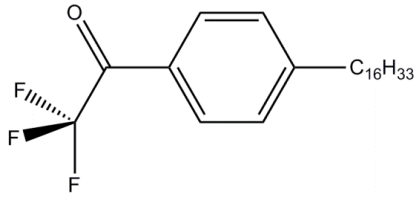
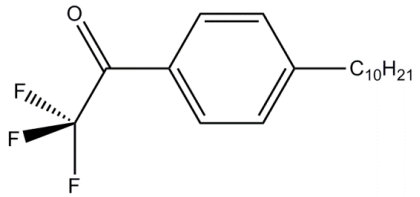
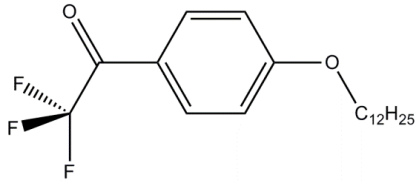
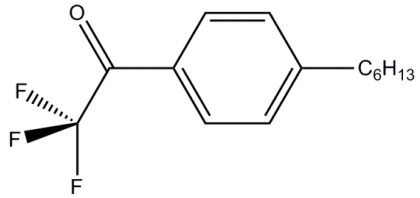
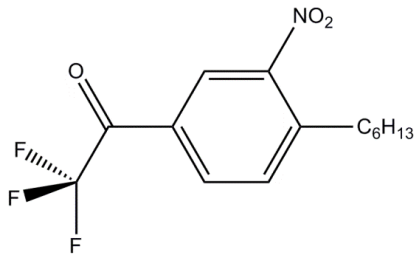
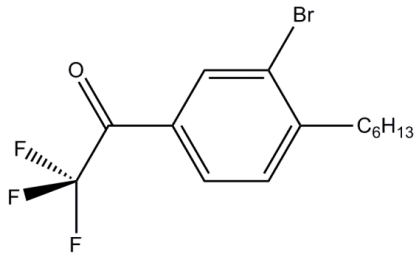
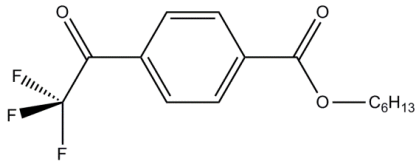
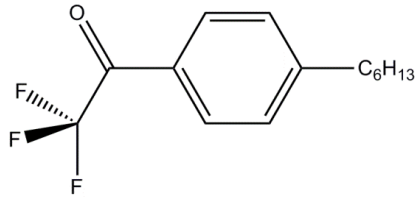
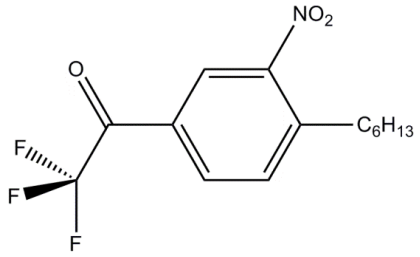
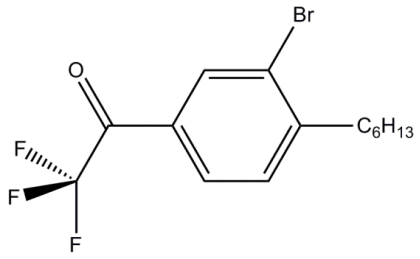
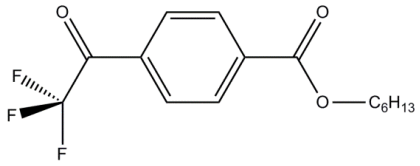
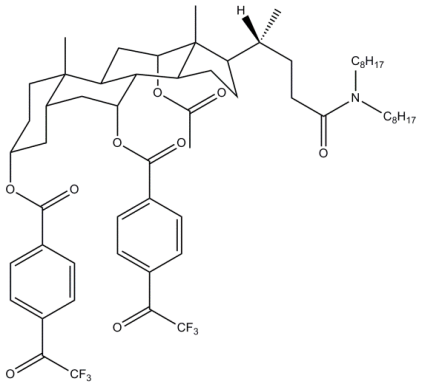
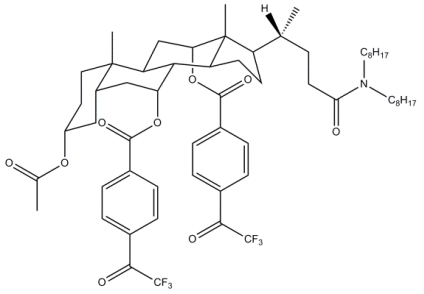
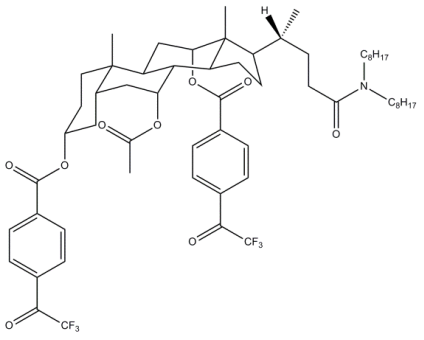
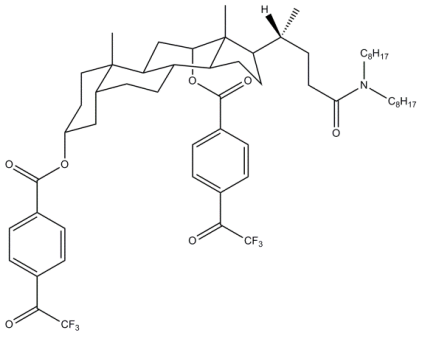
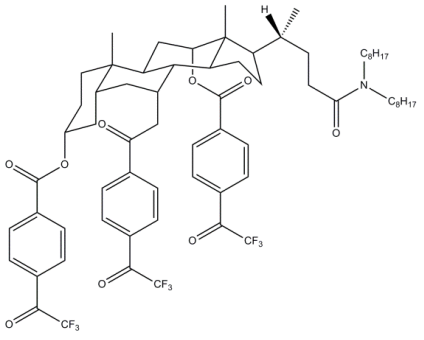
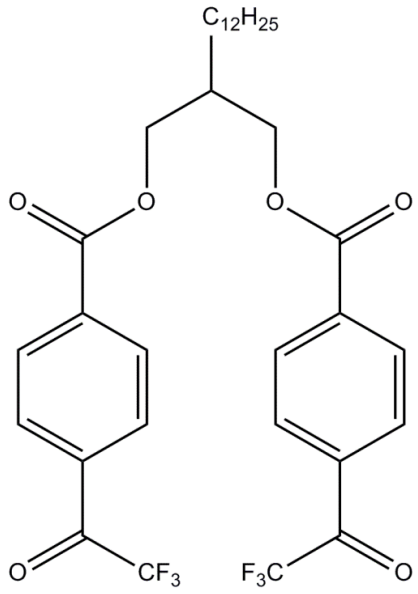
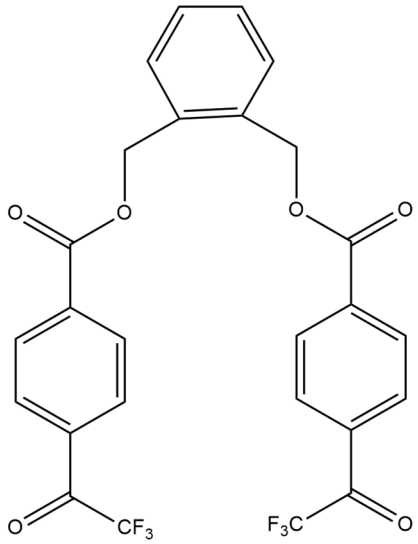
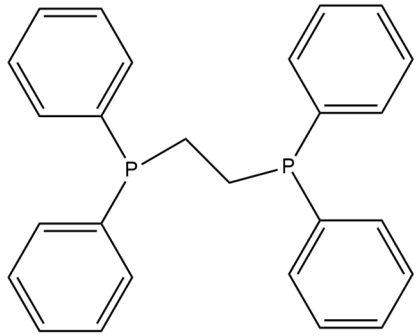
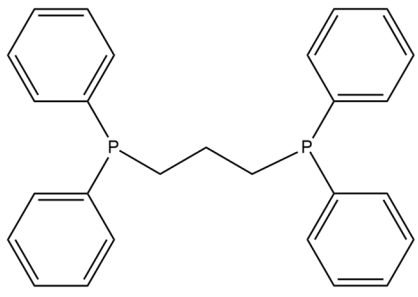
Table S1. Structure and selectivity of the ionophores employed for modeling.

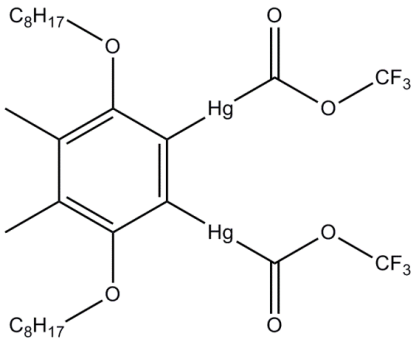
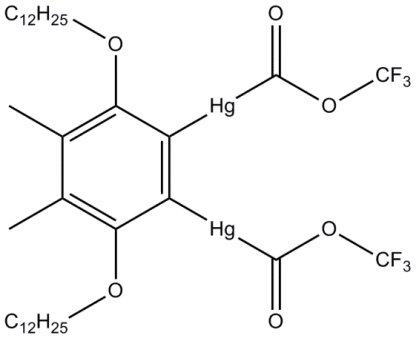
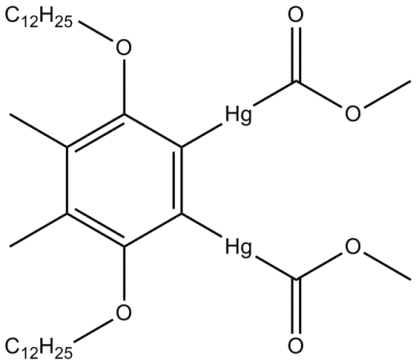
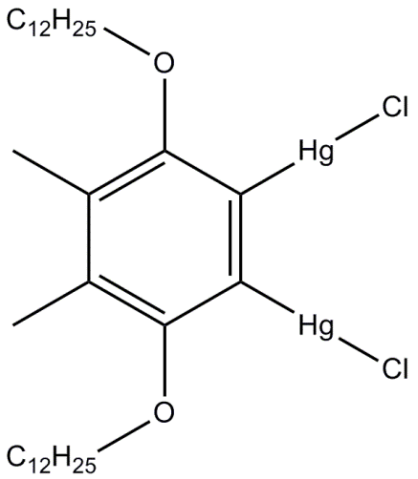
#	Structure of ionophore	Plasticiser	Log K(HCO_3^-/Cl^-)	Reference
1		DOS	−2	[S1]
2		DOS	−1.8	[S2]
3		DOS	−3.2	[S2]
4		DOS	−3.8	[S2]

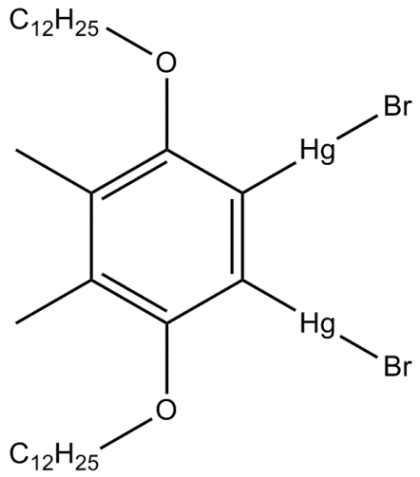
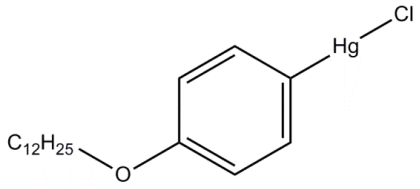
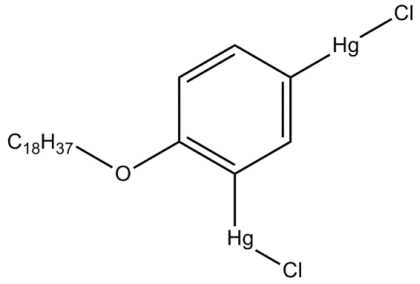
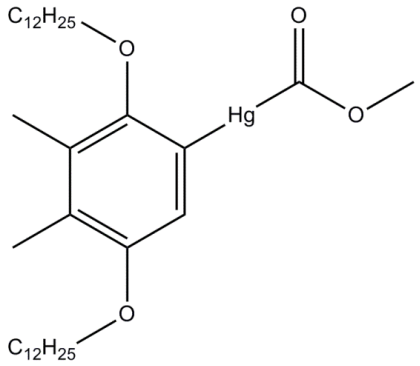
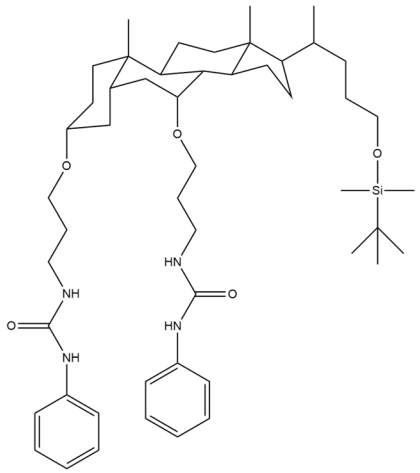
5		DOS	−4	[S2]
6		DOS	−5	[S2]
7		DOS	−4	[S3]
8		DOS	−5	[S2]
9		DOS	−5	[S2]
10		DOS	−2.1	[S1]
11		DOA	−3.7	[S4]
12		DOS	−3	[S1]
13		DOS	−2.8	[S5]

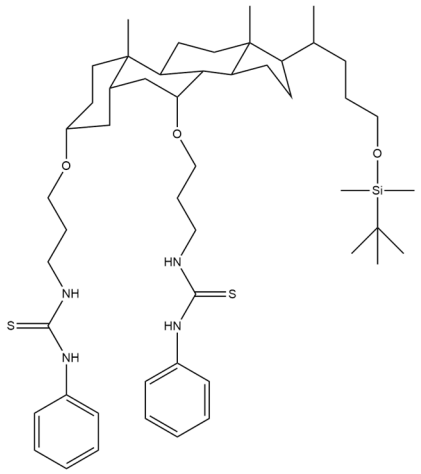
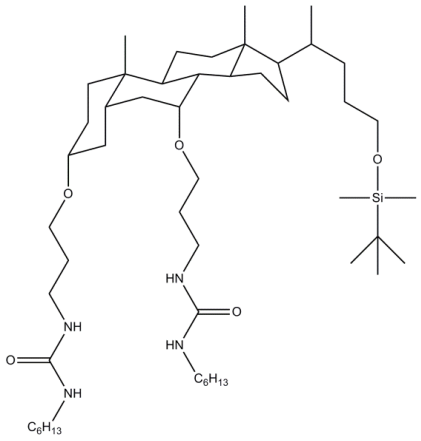
14		DOS	−3	[S5]
15		DOS	−3.2	[S5]
16		DOS	−3.2	[S5]
17		NPOE	−2.4	[S5]
18		NPOE	−2.4	[S5]
19		NPOE	−2.8	[S5]
20		NPOE	−2.6	[S5]

21		DOA	−5.2	[S6]
22		DOA	−4.7	[S6]
23		DOA	−5.7	[S6]
24		DOA	−3.1	[S6]
25		DOA	−5.8	[S6]

26		DOA	−4.2	[S4]
27		DOA	−2.6	[S4]
28		NPOE	1.7	[S7]
29		NPOE	1.6	[S7]

30		DOS	5.5	[S8]
31		DOS	4.9	[S8]
32		DOS	6.2	[S8]
33		DOS	4.8	[S8]

34		DOS	2.8	[S8]
35		DOS	1.4	[S8]
36		DOS	4.5	[S8]
37		DOS	0.2	[S8]
38		NPOE	2.9	[S6]

39		NPOE	1.1	[S6]
40		NPOE	1.3	[S6]

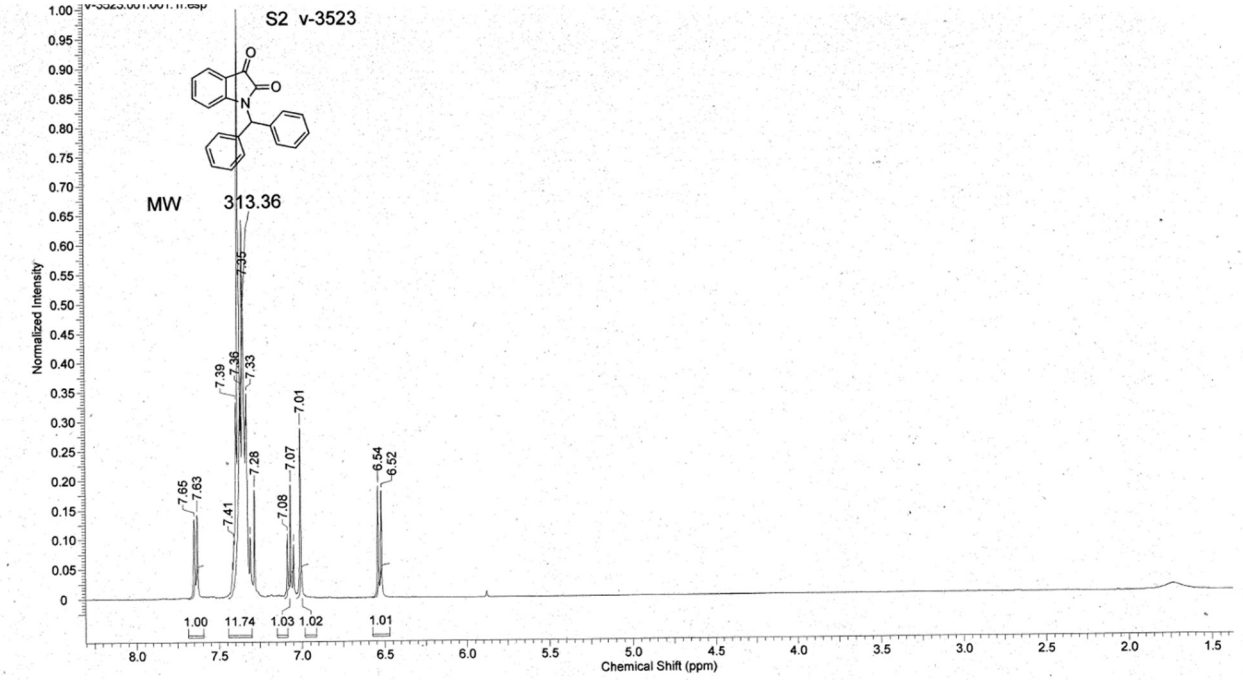
Synthesis of the new ligands.

Phenanthrenequinone, bromodiphenylmethane and oxalyl chloride were purchased from Acros Organics, 2- nitroindan-1,3-dione, 4-chlorodiphenylmethanol and N-benzyl-3,5-dimethoxybenzamide were obtained from Alinda Chemical Trade Company Ltd., all other chemicals and solvents in analytical grade were from JSC Vekton (St. Petersburg, Russia). 1H NMR spectra were recorded using Bruker Avance III 400 MHz Ultrashield Plus spectrometer. Melting points are uncorrected.

Synthesis of S2

1-(diphenylmethyl)-1H-indole-2,3-dione was prepared by slightly modified procedure described in [S9]. The solution of isatin (1.0 g, 6.78 mmol) in anhydrous N,N-dimethylformamide (5 mL) was added dropwise over 30 min to the suspension of hexane-washed sodium hydride (0.34 g, 8.49 mmol) in anhydrous N,N-dimethylformamide (5 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0° C and then the solution of bromodiphenylmethane (1.85 g, 7.45 mmol) in anhydrous N,N-dimethylformamide (2 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm up to the ambient temperature and was stirred for 16 h and heated to 60 °C for 2 h. The mixture was cooled to 0° C and water (1 mL) was carefully added. The mixture was poured into water (25 mL), the precipitated solid was filtered, washed with water (20 mL), dried and recrystallized from cyclohexane. The yield was 1.37 g (64%), m.p. 165–67 °C (literature data m.p. 168 °C [S10])

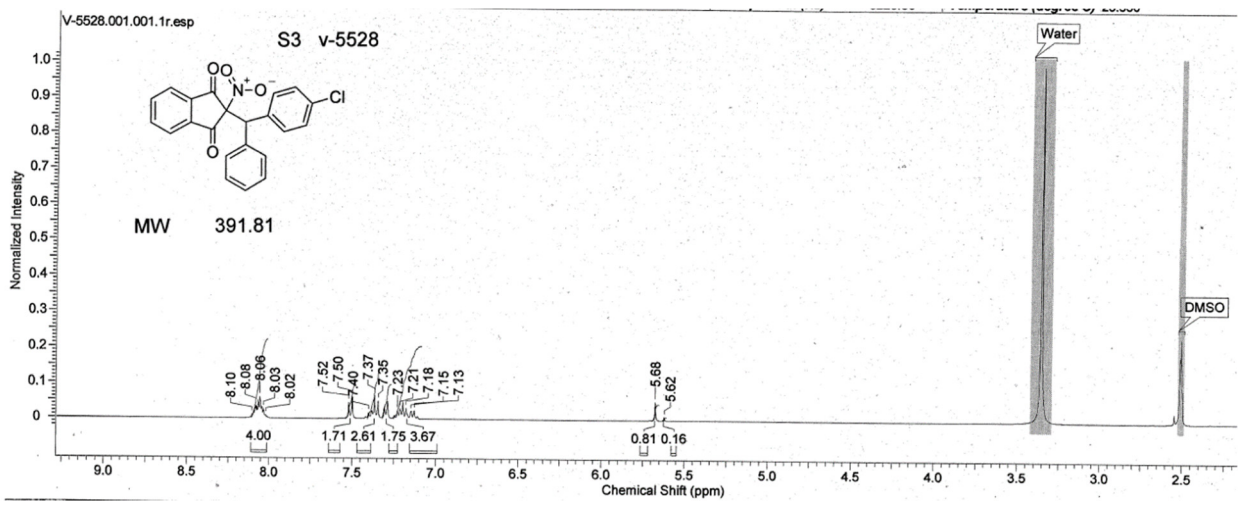
^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.53d (1H, 7-H_{Ar}), 7.01s (1H, CH_{alk}), 7.07t (1H, 6-H_{Ar}), 7.33- 7.41m (11H, 10H_{Ph}+5-H_{Ar}), 7.64 d (1H, 4-H_{Ar})



Synthesis of S3

2-((4-chlorophenyl)(phenyl)methyl)-2-nitro-1H-indane-1,3-dione was prepared by the method described for the synthesis of 2-benzhydryl-2-nitroindan-1,3-dione [S11]. The mixture of 2- nitroindan-1,3-dione (0.96 g, 5 mmol), 4-chlorodiphenylmethanol (1.09 g, 5 mmol) and acetic acid (15 mL) was refluxed for 10 min. The resulting solution was allowed to stand at −10° C for 1 h and then filtered, the residue was washed with water and dried in vacuum. S3 was crystallized from reaction mixture in sufficiently pure state, since its solubility in acetic acid is much lower than that of the initial compounds. As described in the literature on synthesis of 2-benzhydryl-2-nitroindan-1,3-dione [S11], the re-crystallization of the precipitated product did not change its melting point but only led to a significant loss of material. Yield 0.42 g (21%), m.p. 145-147° C

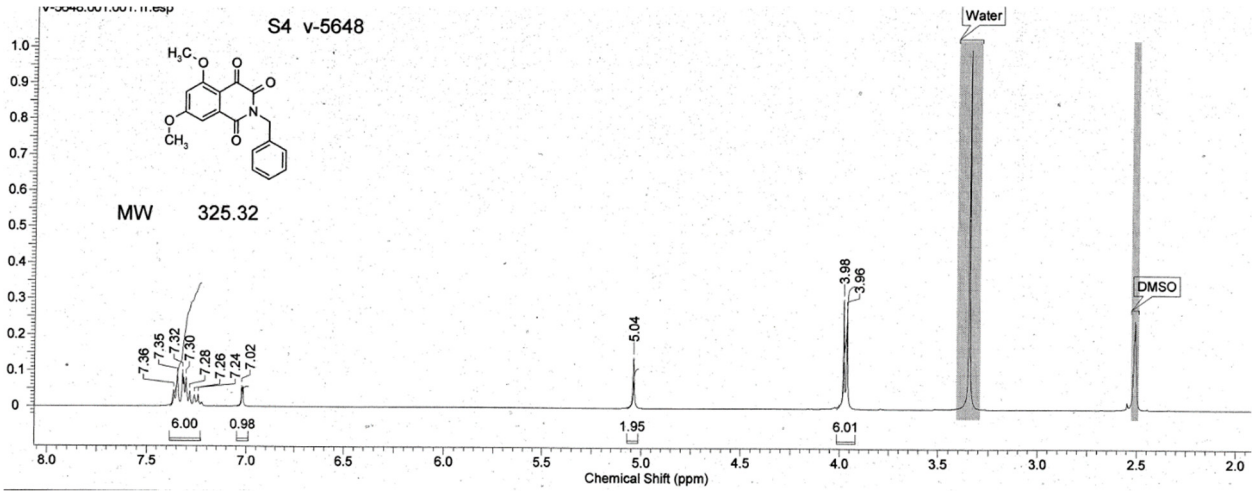
^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm: 3.97d (6H, OCH$_3$), 5.05s (2H, CH$_2$), 7.02s (1H, 6-H$_{Ar}$), 7.33-7.36m (6H, 5H$_{Ph}$+8-H$_{Ar}$)



Synthesis of S4

5,7-dimethoxy-2-benzyl-1,3,4(2H)-isoquinolinetrione was prepared by cyclization of N-benzyl-3.5-dimethoxybenzamide with oxalyl chloride as described for its analogues [S12]. The solution of N-benzyl-3.5-dimethoxybenzamide(1.35 g, 5 mmol) in o-dichlorobenzene (10 mL) was added to the solution of oxalyl chloride(4.25 mL, 6.25 mmol) in o-dichlorobenzene (5 mL) at 60 °C. When no further formation of HCl was observed, the mixture was heated slowly to 140-150 °C and maintained at this temperature for 4 h. The solvent was removed under reduced pressure, a solid residue was crystallized from acetic acid. Yield 0.94 g (58%), m.p. 201–203 °C

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.62s +5.68s (0.17H+0.82H, $CH_{alk,}$ rotamers), 7.15-7.52m (9H, C_6H_5+ClC_6H_4, rotamers), 8.06m (4H, Ar)



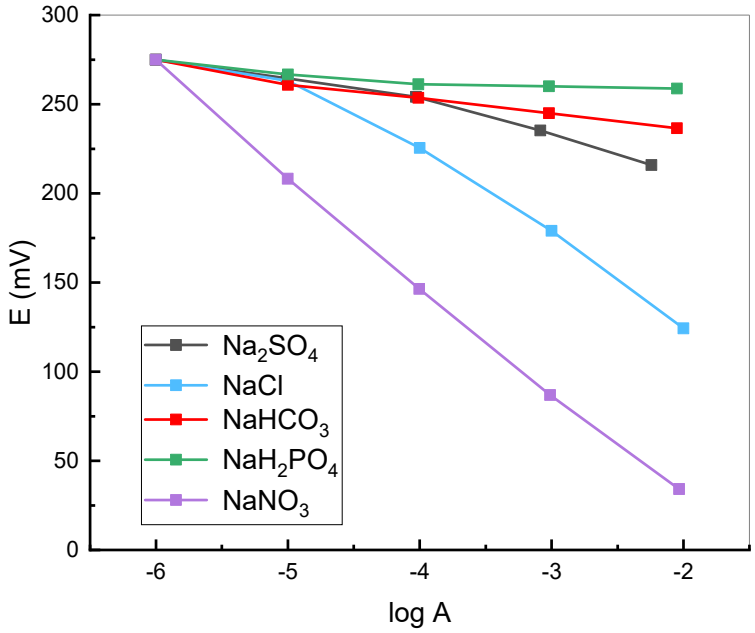


Figure S1. Typical potentiometric response curves of the sensor S2. The EMF readings are offset to zero for better comparability.

Table S2. Sensitivity values of the sensors in the solution of the studied anions, mV/dec.

	SO_4^{2-}	Cl^-	HCO_3^-	$H_2PO_4^-$	NO_3^-
S1	1.7 ± 0.3	−6.4 ± 1.0	−43.4 ± 3.8	29.6 ± 1.1	−27.5 ± 0.9
S2	−16.6 ± 1.1	−41.0 ± 1.2	−7.2 ± 3.4	−1.5 ± 1.2	−57.8 ± 0.8
S3	−24.0 ± 1.6	−42.5 ± 3.8	−16.4 ± 4.2	−3.5 ± 1.4	−64.9 ± 5.9
S4	−1.2 ± 1.2	−23.8 ± 1.0	−28.7 ± 1.6	12.4 ± 1.4	−47.1 ± 0.7

Supplementary References

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