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Supplementary material

SUPPLEMENTARY MATERIAL TO

Solvatochromism of isatin based Schiff bases: An LSER and LFER study

DOMINIK R. BRKIĆ[1], ALEKSANDRA R. BOŽIĆ[1], VESNA D. NIKOLIĆ[2],
ALEKSANDAR D. MARINKOVIĆ[3], HANA ELSHAFLU[3],
JASMINA B. NIKOLIĆ[3]* and SAŠA Ž. DRMANIĆ[3]

[1]Belgrade Polytechnic, Brankova 17, 11000 Belgrade, Serbia, [2]Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, 11000 Belgrade, Serbia and [3]Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

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GENERAL METHOD FOR THE PREPARATION OF ISATIN DERIVATIVES

The isatin derivatives were synthesized according to a literature method.[1] Isatin (5 mmol) was dissolved in methanol (40 mL), and the corresponding reactants (substituted anilines or arylamines (5 mmol) and glacial acetic acid (10 mL) were added. The reaction mixture was refluxed at 70 °C for 6 h using a magnetic stirrer. Subsequently, the mixture was left overnight without stirring at room temperature. The obtained crystals were filtered off, dried and recrystallized from methanol or an appropriate solvent mixture (Table S-I). The average yield was about 70–79 %.

TABLE S-I. Solvent parameters used in Kamlet–Taft Equation[2]

Solvent	π^*	β	α
Ethanol	0.54	0.77	0.83
Methanol	0.6	0.62	0.93
2-Propanol	0.48	0.95	0.76
2-Butanol	0.4	0.8	0.69
Cyclohexanol	0.45	0.84	0.66
Benzyl alcohol (BnOH)	0.98	0.52	0.6
2-Methoxyethanol	0.71	0	0
2-Chloroethanol	0.46	0.53	1.28
1,2-dimethoxyethane (DME)	0.53	0.41	0
Toluene	0.54	0.11	0
Dichloromethane (DCM)	0.82	0.1	0.13
Tetrahydrofuran (THF)	0.58	0.55	0
Acetonitrile (ACN)	0.75	0.31	0.19

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* Corresponding author. E-mail: jasmina@tmf.bg.ac.rs

TABLE S-I. Continued

Solvent	π^*	β	α
Formamide	0.97	0.48	0.71
Dimethylacetamide (DMAc)	0.88	0.76	0
Dimethylformamide (DMF)	0.88	0.69	0
1-Methyl-2-pyrrolidinone (NMP)	0.92	0.77	0
Ethyl acetate (EtOAc)	0.55	0.45	0
2-Pyrrolidone	0.85	0.77	0.36
Dimethyl sulfoxide (DMSO)	1	0.76	0
Acetone	0.71	0.48	0.08
Cyclohexanone	0.76	0.53	0

MATERIALS AND INSTRUMENTATION

All commercially available chemicals were purchased from Sigma–Aldrich (St. Louis, MO, USA). The NMR spectral measurements were performed on a Varian 2000 (200 MHz for ^{1}H- and 50 MHz for ^{13}C-NMR). The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d_6). The chemical shifts are expressed in ppm values referenced to δ_H = 2.5 ppm and δ_C = 39.5 ppm in the ^{1}H- and ^{13}C-NMR spectra, respectively. UV data were recorded on a Shimadzu 1700 UV–Vis spectrophotometer in ethanol as solvent at a concentration of 5×10^{-5} mol dm^{-3}. Fourier-transform infrared (FTIR) spectra were obtained of the samples in the form of KBr pellets using an FTIR Bomem MB 100 instrument. The FTIR spectra were recorded in the transmission mode between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The results of ^{1}H- and ^{13}C-NMR, FTIR spectra and elemental analysis of the studied compounds are given in Table S-II, and the general structure of 1,3-dihydro-3-(arylimino)-2*H*-indol-2-one with labelling of the atoms is given in Fig. S-1.

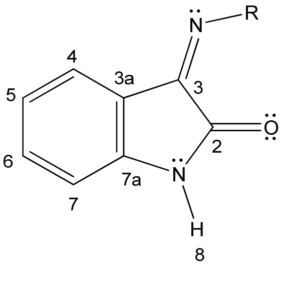


Fig. S-1. General formula of 1,3-dihydro-3-(arylimino)-2*H*-indol-2-one with labelling of the atoms.

TABLE S-II. Yields, melting points, and FTIR, ^{1}H- and ^{13}C-NMR data of the synthesized compounds

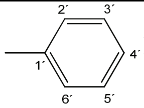
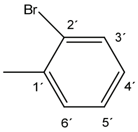
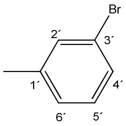
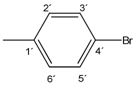
No.	R	Yield and m.p.	IR (cm^{-1})	^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm)	^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm)
1		Yield: 76 %; Exp.: 221–222 °C (methanol) Lit.: 209.7–211.4 °C[3]	3344, 1741, 1661, 1254.	6.65 (1H, *d*, H4), 6.74 (1H, *t*, H5), 6.95 (1H, d, H4′), 7.04 (2H, *d*, H2′ & H6′), 7.26 (1H, *t*, H6), 7.30 (1H, *t*, H7), 7.44 (2H, *t*, H3′ & H5) 10.76 (1H, *s*, H8).	112.1 (C7), 116.4 (C3a), 118.1 (C2′ & 6′), 123.0 (C5), 125.70 (C4), 126.6 (C4′), 129.7 (C3′ & 5′), 134.6 (C6), 146.0 (C7a), 151.88 (C1′), 156.20 (C3), 164.21 (C2).
2		Yield: 69 %; Exp.: 223–224 °C (methanol) Lit.: 219.8–220.6 °C[3]	3342, 1746, 1659, 1252.	6.41 (1H, *d*, H4), 6.38 (1H, *td*, H5), 6.78 (1H, *d*, H6′), 6.94 (1H, *d*, H6), 7.34 (1H, *d*, H4′), 7.36–7.43 (2H, *m*, H7 & H5′), 7.62 (1H, *d*, H3′), 10.66 (1H, *s*, H8).	89.1 (C2′), 111.6 (C7), 116.74 (C3a), 119.58 (C6′), 122.21 (C5), 123.4 C4′), 125.82 (C4), 127.13 (C5′), 133.02 (C3′), 135.11 (C6), 147.62 (C1′), 148.04 (C7a), 152.1 (C3), 164.1 (C2).
3		Yield: 66 %; Exp.: 235–236 °C (methanol) Lit.: 219.1–220.2 °C[3]	3340, 1744, 1658, 1250.	6.38 (1H, *d*, H4), 6.39 (1H, *td*, H5), 6.88 (1H, *d*, H6′), 6.91 (1H, *d*, H6), 7.28 (1H, *d*, H5′), 7.37 (1H, *dd*, H7), 7.54–7.68 (2H, *m*, H2′ & H4′), 10.84 (1H, *s*, H8).	88.56 (C3′), 111.8 (C7), 116.70 (C3a), 119.69 (C6′), 122.24 (C5), 123.4 C2′), 125.77 (C4), 126.23 (C4′), 135.06 (C6), 136.02 (C5′), 147.61 (C1′), 148.2 (C7a), 152.03 (C3), 164.03 (C2).
4		Yield: 80 %; Exp.: 244–241 °C (methanol) Lit.: 220.9–223 °C[3]	3342, 1745, 1648, 1251	6.40 (1H, *d*, H4), 6.71 (1H, *td*, H5), 6.83 (2H, *d*, H2′, 6′), 6.91 (1H, *d*, H6), 7.35 (1H, *dd*, H7), 7.76 (2H, *td*, H3′ & 5′), 10.81 (1H, *s*, H8).	89.55 (C4′), 111.91 (C7), 115.87 (C3a), 119.69 (C2′, C6′), 122.18 (C5), 125.72 (C4), 135.0 (C6), 138.58 (C3′ & C5′), 147.39 (C7a), 147.63 (C1′), 152.09 (C3), 164.11 (C2).

TABLE S-II. Continued

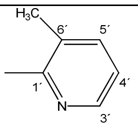
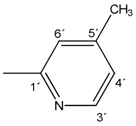
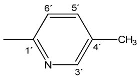
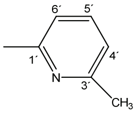
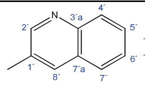
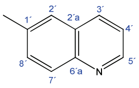
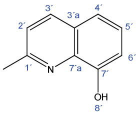
C	R	Yield and m.p.	IR (cm^{-1})	^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm)	^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm)
5		Yield: 64 %; Exp.: 239–240 °C (DMF/ /methanol)	3445, 3191, 1751, 1729, 1625, 1251.	2.31 (3H, *s*, CH_3), 6.41 (1H, *d*, H4), 6.72 (1H, *td*, H5), 6.96 (1H, *d*, H6), 7.06 (1H, *d*, H4′), 7.38 (1H, *dd*, H7), 7.66 (1H, *dd*, H5′), 8.36 (1H, *dd*, H3′), 11.05 (1H, s, H8).	19.7 (CH_3), 111.88 (C7), 115.98 (C3a), 118.73 (C4′), 122.19 (C5), 125.82 (C4), 131.24 (C3′), 135.12 (C6), 138.22 (C5′), 147.44 (C7a), 151.64 (C3′), 152.16 (C3), 158.3 (C1′), 163.4 (C2).
6		Yield: 72 %; Exp.: 204–205 °C (DMF/ /methanol) Lit.: 204–206 °C[1]	3444, 3191, 1752, 1731, 1627, 1254.	2.34 (3H, *s*, CH_3), 6.41 (1H, *d*, H4), 6.68 (1H, *td*, H5), 6.93 (1H, *d*, H6), 7.11 (1H, *d*, H6′), 7.38 (1H, *dd*, H7), 7.45 (1H, *dd*, H4′), 8.42 (1H, *dd*, H3′), 11.04 (1H, *s*, H8).	19.8 (CH_3), 111.91 (C7), 115.99 (C3a), 117.90 (C6′), 122.19 (C5), 125.68 (C4), 127.3 (C4′), 135.13 (C6), 147.38 (C7a), 148.58 (C5′), 151.44 (C3′), 152.32 (C3), 155.32 (C1′), 163.4 (C2).
7		Yield: 60 %; Exp.: 203–204 °C (DMF/ /methanol)	3447, 3193, 1753, 1733, 1626, 1253.	2.33 (3H, *s*, CH_3), 6.43 (1H, *d*, H4), 6.72 (1H, *td*, H5), 6.88 (1H, *d*, H6′), 6.95 (1H, *d*, H6), 7.37 (1H, H, H7), 7.63 (1H, *dd*, H5′), 8.33 (1H, *dd*, H3′), 11.07 (1H, *s*, H8).	19.5 (CH_3), 111.88 (C7), 116.01 (C3a), 117.73 (C6′), 122.22 (C5), 125.74 (C4), 132.3 (C4′), 135.1 (C6), 138.58 (C5′), 147.41 (C7a), 151.74 (C3′), 152.2 (C3), 154.4 (C1′), 163.6 (C2).
8		Yield: 71 %; Exp.: 185–187 °C (DMF/ methanol)	3447, 3191, 1753, 1731, 1626, 1253.	2.30 (3H, *s*, CH_3), 6.43 (1H, *d*, H4), 6.74 (*td*, 1H, 5), 6.88 (*d*, 1H, 6), 6.94 (1H, *d*, H6′), 7.40 (1H, *dd*, H7), 7.68 (1H, *dd*, H5′), 7.72 (1H, *dd*, H4′), 11.03 (1H, *s*, H8).	19.4 (CH_3), 111.92 (C7), 116.01 (C3a), 114.73 (C6′), 122.26 (C5), 123.42 (C4′), 125.91 (C4), 135.22 (C6), 137.50 (C5′), 147.51 (C7a), 151.62 (C3′), 152.18 (C3), 156.42 (C1′), 163.5 (C2).

TABLE S-II. Continued

C	R	Yield and m.p.	IR (cm^{-1})	^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm)	^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm)
9		Yield: 59 %; Exp.: 300–301 °C (DMF/ /methanol) Lit.: 303–304 °C[4]	3048,1742, 1614, 1311, 1254.	6.33 (1H, *d*, H4), 6.69 (1H, *td*, H5), 6.92 (1H, *d*, H6), 7.11 (1H, *t*, H6′), 7.35 (1H, *dd*, H7), 7.44–7.82 (2H, *dtdd*, H4′ & H5′), 7.87–8.15 (2H, *m*, H7′ & H8′), 8.68 (1H, *dd*, H2′), 11.03 (1H, *s*, H8).	111.34 (C7), 116.20 (C3a), 122.33 (C5), 125.52 (C4), 127.79 (C6′), 128.11 (C4′), 128.30 (C5′), 128.50 (C8′), 129.20 (C7′a), 135.11 (C7′), 135.34 (C6), 143.11 (C2′), 144.51 (C1′), 146.53 (C3′a), 147.70 (C7a), 154.25 (C3), 163.52 (C2).
10		Yield: 64 %; Exp.: 290–291 °C (DMF/ /methanol)	3061,1742, 1618, 1302, 1254.	6.35 (1H, *d*, H4), 6.72 (1H, *td*, H5), 6.94 (1H, *d*, 6H), 7.30 (1H, *t*, H7′), 7.37 (1H, *dd*, H7), 7.52–7.85 (2H, *m*, H4′ & H8′), 8.09–8.40 (2H, *m*, H2′ & H3′), 8.79 (1H, *dd*, H5′), 11.06 (1H, *s*, H8).	111.28 (C7), 115.9 (C3a), 122.29 (C5), 125.47 (C4), 126.76 (C2′), 127.66 (C4′), 128.10 (C8′), 129.80 (C2′a), 133.10 (C7′), 135.11 (C3′), 136.56 (C6), 146.98 (C6′a), 147.54 (C7a), 149.11 (C5′), 151.11 (C1′), 154.31 (C3), 163.8 (C2).
11		Yield: 70 %; Exp.: 283–285 °C (DMSO/ /methanol)	3451, 3056, 1740, 1626, 1302.	6.33 (1H, *d*, H4), 6.67 (1H, *t*, H5), 6.92 (1H, *d*, H6), 7.35 (1H, *t*, H5′), 7.45–7.61 (3H, *m*, H7, H4′ & H6′), 8.14 (1H, *d*, H3′), 8.35 (1H, *d*, H2′), 9.80 (1H, *d*, H8′), 11.06 (1H, *s*, H8).	111.24 (C7). 112.00 (C6′), 116.13 (C3a). 117.71 (C4′), 118.65 (C2′), 122.41 (C5), 125.58 (C4), 127.97 (C5′), 128.71 (C3a′), 135.41 (C6), 136.03 (C3′), 138.10 (C7a′), 147.70 (C7a), 153.36 (C1′), 159.25 (C3), 163.52 (C2), 175.72 (C7′).

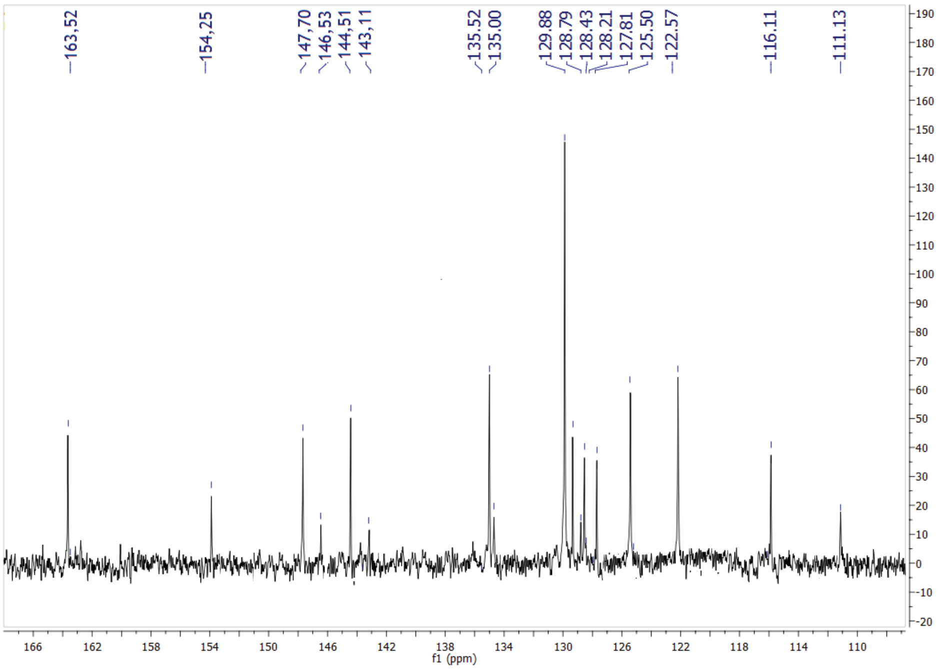


Fig. S-2. ^{1}H-NMR spectrum of compound **9**.

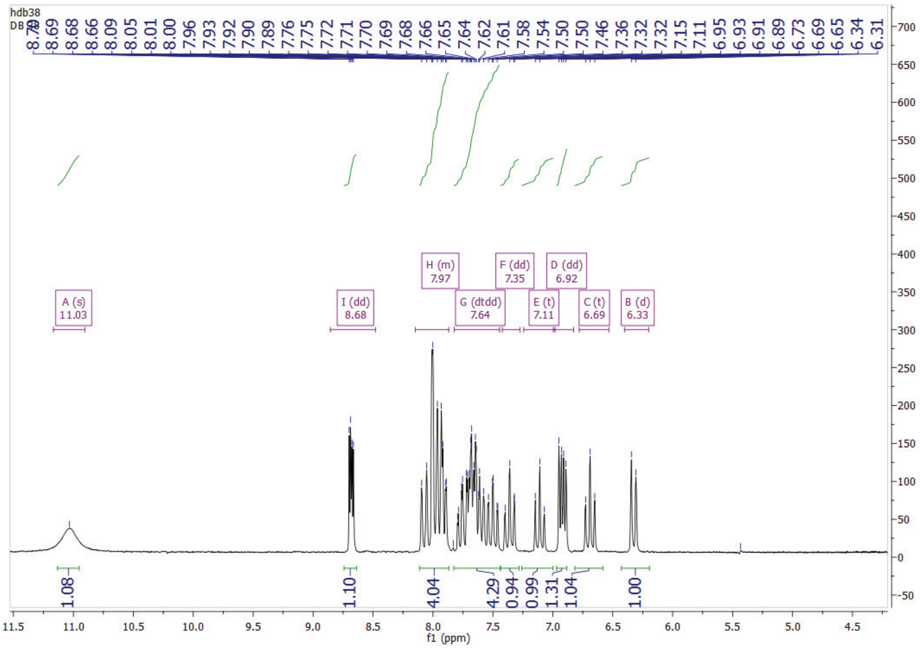


Fig. S-3. ^{13}C-NMR spectrum of compound **9**.

TABLE S-III. Absorption frequencies ($\nu_{\max}\times10^{-3}$ / cm^{-1}) of isatin compounds in selected solvents (lower wavelength peak)

Solvent	Compound										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Methanol	34.31	33.39	33.5	33.44	33.39	33.73	33.61	33.73	32.63	33.9	34.01
Ethanol	33.17	33.28	33.44	33.17	33.22	33.39	33.33	33.39	31.5	34.07	33.22
2-Propanol	33.50	33.67	33.67	33.61	33.28	33.61	33.61	33.67	33.11	–	33.96
2-Butanol	–	–	–	–	–	–	–	–	31.35	–	–
Cyclohexanol	–	–	–	–	–	–	–	–	–	–	–
Benzyl alcohol (BnOH)	–	–	–	–	31.7	–	–	–	–	31.06	–
2-Methoxyethanol (2-ME)	–	33.44	33.44	33.5	33.5	33.06	33.56	33.78	32.79	34.01	33.78
2-Chloroethanol (2-CE)	–	33.11	33.06	33.28	32.89	33.06	33.06	33.28	32.73	–	32.73
DME	–	34.01	33.78	33.96	34.19	34.25	34.07	34.07	31.3	34.19	34.36
Toluene	–	33.73	33.61	33.78	–	–	–	–	31.15	31.4	33.33
DCM	–	33.67	33.73	33.61	–	33.73	33.61	33.78	32.95	34.19	33.9
Acetone	–	–	–	–	–	–	–	–	–	–	–
Cyclohexanone	–	–	–	–	–	–	–	–	–	–	–
EtOAc	35.03	34.01	33.9	34.07	–	34.13	34.13	34.19	31.4	34.42	34.48
Formamide	–	33.22	33.17	33.11	33.17	33.22	33.22	33.22	32.36	33.84	33.84
DMF	–	33.56	33.44	33.56	34.13	33.67	33.73	33.73	31.4	34.19	34.25
DMAc	36.30	33.67	33.67	33.67	33.73	33.73	33.61	33.78	31.3	34.25	34.25
NMP	–	33.61	33.39	33.56	–	33.78	33.56	33.61	31.2	34.19	34.07
ACN	35.97	33.84	33.96	34.01	–	33.9	33.9	33.90	32.84	34.54	34.36
DMSO	–	33.5	33.56	33.73	33.73	33.61	33.61	33.67	31.25	34.13	34.01
THF	36.83	33.84	33.73	33.67	34.25	34.13	34.07	34.13	31.3	34.25	34.25
2-Pyrrolidone	–	33.67	33.67	33.67	33.5	33.73	33.61	33.61	31.45	34.42	34.01

TABLE S-IV. The results of the correlation analysis for the isatin derivatives (lower wavelength peak) according to the Kamlet–Taft Equation; no statistically valuable correlations were obtained for compds. **1** and **10**

Compd.	ν_0	s	b	a	R[a]	SD[b]	F[c]	P_π[d]	P_β[d]	P_α[d]	Solvent excluded from the correlation
	$\times10^{-3}$ cm^{-1}							%			
2	34.50 ±0.16	–0.86 ±0.18	–0.13 ±0.15	–0.62 ±0.08	0.94	0.11	24.99	53.42	8.07	38.51	2-Butanol, cyclohexanol, BnOH, Acetone, ChO, 2-methoxyethanol, toluene, 2-pyrrolidone
3	33.89 ±0.11	–0.66 ±0.15	0.55 ±0.12	–0.57 ±0.07	0.95	0.09	23.96	37.08	30.90	32.02	2-Butanol, cyclohexanol, BnOH, acetone, ChO, ACN, DCM, NMP, DMF, methanol
4	34.37 ±0.13	–0.93 ±0.17	0.18 ±0.14	–0.57 ±0.08	0.94	0.10	21.35	55.36	10.71	33.93	2-Butanol, cyclohexanol, BnOH, acetone, ChO, ACN, ethanol, THF, 2-methoxyethanol, 2-pyrrolidone

TABLE S-IV. Continued

Compd.	ν_0	s	b	a	R[a]	SD[b]	F[c]	P_{π}[d]	P_{β}[d]	P_{α}[d]	Solvent excluded from the correlation
	×10^{-3} cm^{-1}							%			
5	35.04 ±0.16	–1.21 ±0.20	–0.33 ±0.16	–0.31 ±0.11	0.94	0.10	18.86	65.41	17.84	17.76	2-Butanol, cyclohexanol, BnOH, toluene, acetone, ChO, F, 2-methoxyethanol, 2-chloroethanol, ethanol
6	34.72 ±0.15	–0.99 ±0.17	–0.05 ±0.14	–0.83 ±0.08	0.96	0.11	40.38	52.94	2.67	44.39	2-Butanol, cyclohexanol, BnOH, toluene, acetone, ChO, 2-methoxyethanol, methanol
7	34.63 ±0.16	–0.97 ±0.18	–0.06 ±0.16	–0.77 ±0.08	0.95	0.11	30.14	53.89	3.33	42.78	2-Butanol, cyclohexanol, BnOH, toluene, acetone, ChO, methanol, 2-methoxyethanol
8	34.63 ±0.12	–1.00 ±0.15	0.02 ±0.10	–0.71 ±0.07	0.96	0.09	39.98	57.80	1.16	41.04	2-Butanol, cyclohexanol, BnOH, toluene, acetone, ChO, methanol
9	31.66 ±0.21	1.57 ±0.28	–2.45 ±0.18	1.42 ±0.13	0.98	0.15	80.32	28.86	45.04	26.10	Cyclohexanol, BnOH, acetone, ChO, 2-propanol, ACN, F, ethanol, toluene
11	34.62 ±0.27	–1.00 ±0.36	0.67 ±0.22	–1.32 ±0.16	0.94	0.18	24.79	33.44	22.41	44.15	2-Butanol, cyclohexanol, BnOH, acetone, ChO, methanol, toluene, F, AcN

[a]Correlation coefficient; [b]standard deviation; [c]Fisher test of significance; [d]the percentage contribution of solvatochromic parameters obtained using the Kamlet–Taft Equation (%)

TABLE S-V. Substituent constants[5]

No.	X	σ
1	H	0
2	2-Br	0.58
3	3-Br	0.39
4	4-Br	0.23
5	3-Me-2-pyridyl	0.63[a]
6	4-Me-2-pyridyl	0.68[a]
7	5-Me-2-pyridyl	0.58[a]
8	6-Me-2-pyridyl	0.68[a]
9	3-Quinolinyl	0.5
10	6-Quinolinyl	0.6
11	8-OH-2-quinolinyl	0.47[a]

[a]The σ constants were calculated as additive values; 4-NO_2 (0.78) and 4-CN (0.66) were taken from the literature[1]

TD-DFT calculations

In order to confirm validity of implemented theoretical consideration, theoretical absorption spectra of compound 1 were calculated in acetone, acetonitrile, ethanol, tetrahydrofuran, dimethylsulfoxide, foramide and toluene. The calculated value for the higher wavelength peak are presented in Table S-VI and are in good agreement with experimental values.

TABLE S-VI. Calculated and experimental absorption frequencies ($\nu_{\rm max}\times10^{-3}$ / cm^{-1}) of compound **1** in selected solvents (higher wavelength peak)

Solvent	Calculated (TD-DFT)	Experimetal
Acetone	24.10	24.66
Acetonitrile	24.13	25.41
Ethanol	24.11	24.48
THF	23.97	23.95
DMSO	24.12	24.39
Formamide	24.13	24.84
Toluene	23.66	24.04

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