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SYNTHESIS OF PYRIDINIUM BETAINE AZO CHROMOPHORES

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New chromophores have been synthesized and investigated containing as acceptor a quaternized pyridine unit with mobile bromine in the structure conjugated with two donor units – the indan-1,3-dione anion and the dihydroxyethylamino group through a π-conjugated spacer.

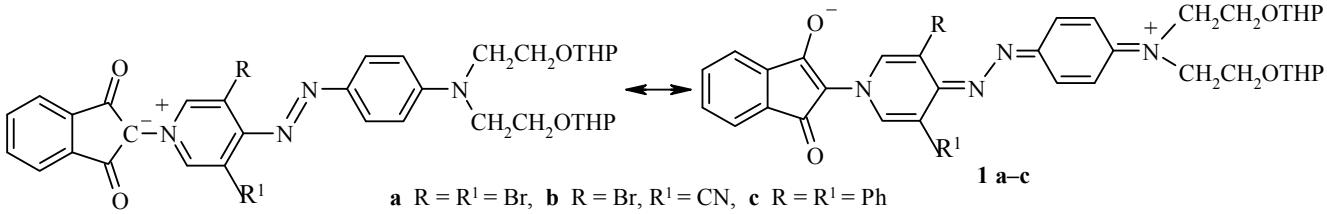
Keywords: azo compounds, chromophore, indane-1,3-dione, pyridine.

Organic nonlinear optical (NLO) materials have the potential for various applications in the field of optical signal processing, giving the impulse to design more and more chromophores with enhanced NLO properties [1].

Among the most investigated subjects are azobenzene derivatives particularly "push-pull" azobenzenes with asymmetric electron distribution because of the substitution pattern at the 4 and 4' positions with electron-releasing (donor, D) and electron-withdrawing (acceptor, A) groups. Due to their large dipole moments and photochemistry (*trans* to *cis* isomerization), they have been investigated as components for NLO devices, lithography, all-optical switches, and data storage [2]. Incorporation of the π-deficient pyridine moiety as acceptor by noncovalent interactions (hydrogen bonds) gives additional advantage to obtain liquid crystals [3], liquid crystalline polymers [4], proton-responsive photo switches [5], and three-dimensional octupolar structures by complexation to transition metals [6].

Azopyridine-based chromophores could be bound covalently to functionalized surfaces by reaction with alkyl- or benzyl halides, simultaneously creating the pyridinium group [7, 8]. Quaternization of pyridine provides a way of enhancing its acceptor capability. Recently, potential NLO and electro-optical properties have been demonstrated for several pyridinium intramolecular salts [9, 10], including N-(1,3-dioxoindan-2-yl)pyridinium betaine (IPB) [11].

In order to extend the scope of compounds with NLO activity, we aim to synthesize the dual chromophore **1** by linking the azopyridine-based chromophore with IPB *via* the common pyridinium moiety. The dioxyethylamino substituent in compound **1** makes it useful for synthesis of polymers. The constitution of molecule **1** can be described by two important mesomeric formulas:



1 a–c

a R = R[1] = Br, **b** R = Br, R[1] = CN, **c** R = R[1] = Ph
THP = tetrahydro-2H-pyran-2-yl

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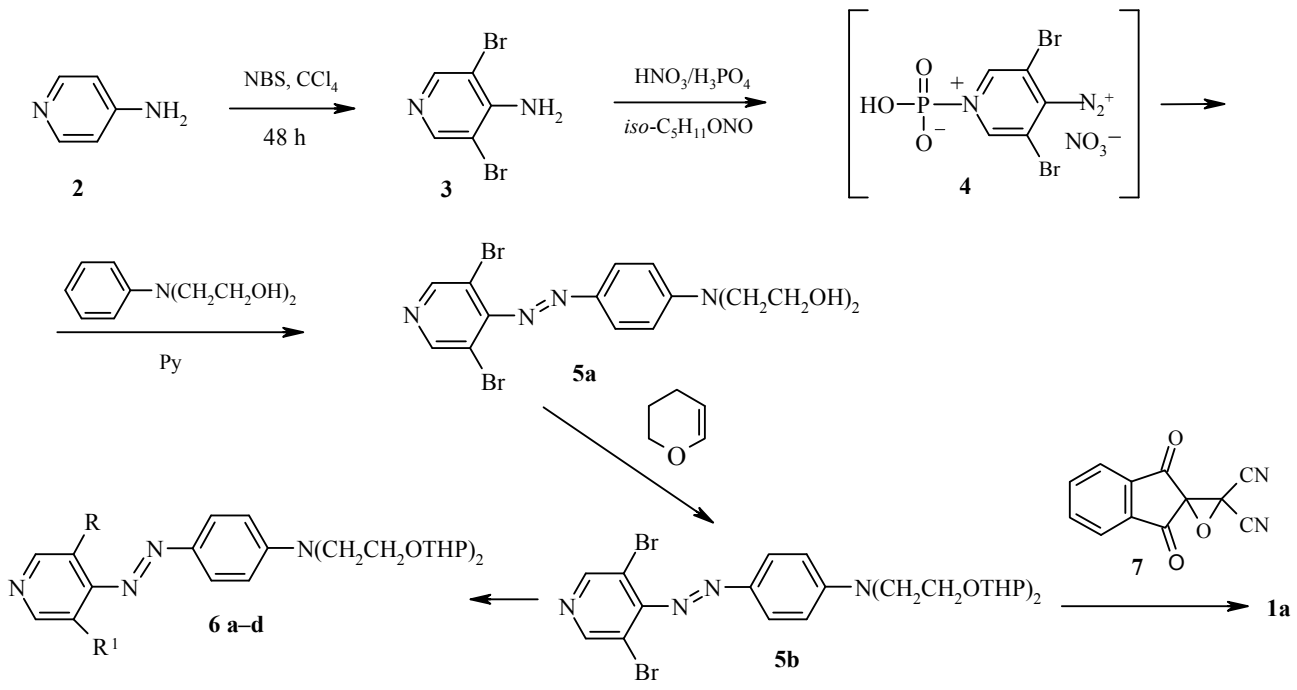
Chromophore **1a** was synthesized from 4-aminopyridine (**2**) as shown in the following scheme:



6a R = Br, R^1 = CN; **b** R = R^1 = CN; **c** R = R^1 = Ph; **d** R = CN, R^1 = Ph

Compound **2** was brominated with NBS in CCl_4 [12] to give 3,5-dibromopyridine-4-amine (**3**). Diazotization of compound **3** was performed by altering the procedure used previously [8] for diazotization of compound **2**, which allowed the formation of amphionic structure **4**, possessing a higher electron density at C-4 in comparison with the protonated diazonium salt, and higher stability [13]. Compound **4** was generated by *iso*-amylnitrite in a mixture of H_3PO_4 and HNO_3, then coupled with N,N-bis(2-hydroxyethyl)aminobenzene in pyridine to yield azo compound **5a**, which was converted to tetrahydro-2H-pyran-2-yl derivative **5b** under standard conditions.

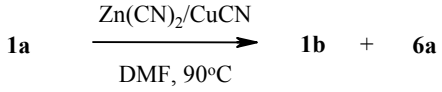
The bromine atoms in compound **5** activated through azophenyl substitution are capable of gradual substitution: in the reaction of compound **5b** with 1 eq. of $Zn(CN)_2$ under catalysis of CuCN, compound **6a** was obtained as the main product, but with 2 eq. of CuCN – compound **6b**. Palladium-catalyzed bis(arylation) of **5b** and **6a** with phenylboronic acid using Suzuki's procedure yielded compounds **6c** and **6d**, respectively.

In order to obtain compound **1,** we examined two methods available in the literature for synthesis of indan-1,3-dione pyridinium betaine [11]: 1) Based on condensation of phthalic anhydride with N-(carboxymethyl)pyridinium salts in the presence of Ac_2O and triethylamine; 2) Based on reaction of pyridine with 2-dicyanomethyleneindan-1,3-dione oxide (**7**). To apply the first method, the N-(carboxymethyl)pyridinium derivative of compound **5** was required. In several attempts to prepare it by the reaction of ethyl or *tert*-butyl 2-iodo- or 2-bromoacetate with compound **5a,** only mixtures of very hygroscopic salts were obtained; therefore the second method for synthesis of compound **1a** was used.

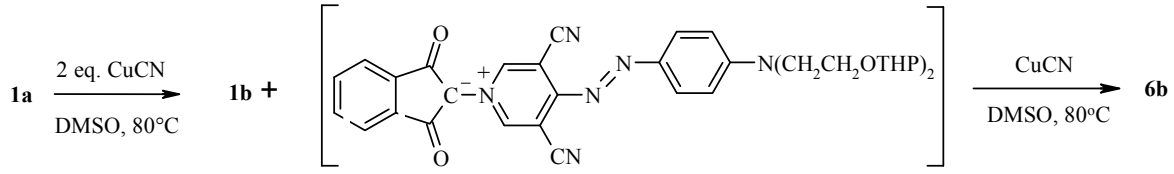
Reaction of compound **5b** with oxide **7** proceeded in boiling MeCN for 4–5 h, and good yields of compound **1a** were obtained. Similarly, reaction of oxide **7** with azo compound **6c** resulted in chromophore **1c**. However, compound **6b** failed to react with oxide **7**, which can be ascribed to the low basicity of the pyridyl group due to the presence of several strong acceptors in the molecule. In the case of the reaction of compound **6a** with oxide

7, low yields of compound **1b** were obtained together with starting material **6a**. TLC chromatography allowed monitoring the partial conversion of compound **6a** into compound **1b**, which during heating lost the indan-1,3-dione fragment and gave back compound **6a**. No sign of decomposition in solutions of compounds **1a** and **1c** could be observed at temperatures below 100°C in the absence of air oxygen.

With better yield, compound **1b** was prepared by treatment of compound **1a** with $Zn(CN)_2$ under the catalysis of CuCN.



As a side product, compound **6a** was formed, which confirmed the low thermal stability of compound **1b** in solution. If compound **1a** was allowed to react with 2 eq. of CuCN in DMSO at 80°C, only compound **6b** was isolated from the reaction mixture.



In the crystalline state compounds **1a-c** are stable. In solution they are subjected like IPB [11] to photochemical oxidation by air.

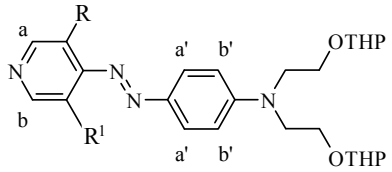
The new chromophores **1a-c**, **5a,b**, and **6a-d** were characterized by elemental analysis (Table 1), ^{1}H NMR (Table 2 and 3), UV-vis spectra (Table 4 and 5), and MS. All data were consistent with the assigned structures.

In the visible region of the UV-vis spectrum, compounds **5b** and **6a-d,** like other *D-π conjugated system-A* type or "push-pull" chromophores, exhibit an intense charge-transfer band with maxima in EtOH at 427 to 543 nm depending on the electron-releasing or -withdrawing character of substituents in the pyridine ring and showing a positive solvatochromic effect at 10-20 nm (from PhMe to EtOH).

TABLE 1. Physical and Analytical Data of Azo Compounds **5a,b** and **6a-d** and Betaines **1a-c**

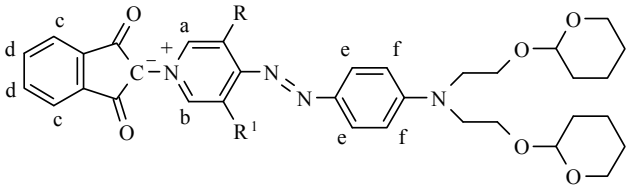
Com-pound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
5a	$C_{15}H_{16}Br_2N_4O_2$	41.09 / 40.57	3.84 / 3.63	12.51 / 12.62	166-169	69
5b	$C_{25}H_{32}Br_2N_4O_4$	49.28 / 49.03	5.23 / 5.27	9.14 / 9.15	100-102	83
6a	$C_{26}H_{32}BrN_5O_4$	56.04 / 55.92	6.23 / 5.78	12.03 / 12.54	108-110	33
6b	$C_{27}H_{32}N_6O_4$	63.95 / 64.27	6.32 / 6.39	16.24 / 16.66	109-111	45
6c	$C_{37}H_{42}N_4O_4$	72.80 / 73.24	6.23 / 6.98	8.76 / 9.23	78-80	64
6d	$C_{32}H_{37}N_5O_4$	69.12 / 69.17	6.32 / 6.71	12.43 / 12.60	68-72	43
1a	$C_{34}H_{36}Br_2N_4O_6$	54.08 / 53.98	4.95 / 4.80	7.48 / 7.41	184-185	48
1b	$C_{35}H_{36}BrN_5O_6$	59.73 / 59.83	5.08 / 5.16	9.89 / 9.97	211	45
1c	$C_{46}H_{46}N_4O_6$	73.13 / 73.58	6.03 / 6.17	7.36 / 7.46	157-158	43

TABLE 2. ^{1}H NMR Spectral Data of Synthesized Azo Compounds **5b** and **6a-d**



Compound	Chemical shifts of protons ($CDCl_3$), δ, ppm (*J*, Hz)					
	H_a, s	H_b, s	$H_{a'}$, d	$H_{b'}$, d	OCHO, t	Other protons
5b	8.59	8.59	7.83 ($J_{a',b'}$ = 9.2)	6.79 ($J_{b',a'}$ = 9.2)	4.54 (J = 3.4)	3.95-3.38 (12H, m), 1.70-1.47 (12H, m)
6a	8.84	8.70	7.92 ($J_{a',b'}$ = 9.2)	6.80 ($J_{b',a'}$ = 9.2)	4.53 (J = 3.5)	3.94-3.40 (12H, m), 1.71-1.50 (12H, m)
6b	8.89	8.89	7.99 ($J_{a',b'}$ = 9.3)	6.85 ($J_{b',a'}$ = 9.3)	4.53 (J = 3.7)	4.03-3.46 (12H, m), 1.76-1.47 (12H, m)
6c	8.59	8.59	7.35 ($J_{a',b'}$ = 9.3)	6.65 ($J_{b',a'}$ = 9.3)	4.55 (J = 3.7)	7.72-7.17 (10H, m), 3.92-3.37 (12H, m), 1.76-1.51 (12H, m)
6d	8.81	8.77	7.73 ($J_{a',b'}$ = 9.2)	6.73 ($J_{b',a'}$ = 9.2)	4.52 (J = 3.7)	7.45-7.35 (5H, m), 3.91-3.39 (12H, m), 1.76-1.46 (12H, m)

TABLE 3. ^{1}H NMR Spectral Data of Synthesized Compounds **1a–c**



Compound	Chemical shifts of protons ($CDCl_3$), δ, ppm (*J*, Hz)							
	H_a	H_b	H_c, m	H_d, m	H_e, d	H_f, d	OCHO, br.	Other protons
1a	10.48 (s)	10.48 (s)	7.53-7.47	7.45-7.39	7.85 (J = 9.2)	6.82 (J = 9.2)	4.53	3.96-3.40 (12H, m), 1.68-1.47 (12H, m)
1b	10.56 (d, J = 1.2)	10.45 (d, J = 1.2)	7.55-7.52	7.46-7.41	7.97 (J = 9.3)	6.61 (J = 9.3)	4.51	3.96-3.38 (12H, m), 1.68-1.47 (12H, m)
1c	10.02 (s)	10.02 (s)	7.51-7.44	7.42-7.35	7.25 (J = 9.2)	6.60 (J = 9.2)	4.49	7.31 (10H, br.), 3.87-3.37 (12H, m), 1.69-1.45 (12H, m)

Compounds **1a–c** could be considered as D^-**–** A^+-π *conjugated system-D* type chromophores. They exhibit two absorption bands: I) A band near 420-460 nm, which can be assigned [11] to electron transfer from the weak donor, indan-1,3-dione anion, to pyridinium cation; II) A more intense band near 520-675 nm associated with charge transfer from the strong dioxyethylamino donor to the pyridinium cation (for example, λ_{max} of 4-dimethylamino-1-(pyridine-4-ylazo)benzene is 580 nm in benzene [14]). The second maximum is red-shifted by 140 (**1a**), 169 (**1b**), and 103 nm (**1c**) in comparison with azo compounds **5b, 6a**, and **6c**, giving evidence of increased charge

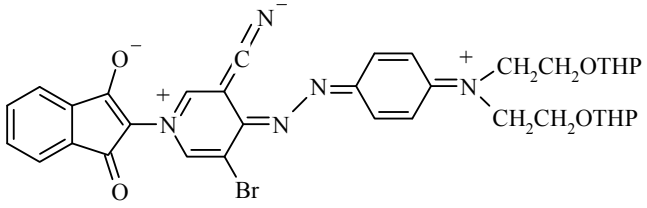
TABLE 4. UV-vis spectra of synthesized Azo Compounds **5a,b, 6a-d** and Betaines **1a-c**

Com-pound	λ_{max}, nm (log ε), in ethanol		λ_{max}, nm, in PhMe	Solvatochromic effect $\lambda_{max\ EtOH} - \lambda_{max\ PhMe}$
5b	269 (3.95)	427 (4.34)	417	10
6a	288 (3.94)	506 (4.46)	486	20
6b	295 (4.07)	543 (4.62)	523	20
6c	270 (4.03)	418 (4.43)	407	11
6d	265 (4.08)	484 (4.45)	467	17
1a	246 (4.66), 284 (4.35)	567 (4.68), 466 (sh, 4.49)	559, 459 (sh)	8
1b	250 (4.50), 297 (4.29)	674 (4.71), 418 (4.15)	657, 426	18
1c	246 (4.73), 300 (4.18)	521 (4.64)	522, 442 (sh)	–1

TABLE 5. Solvent Effect on the Visible Absorption Band λ_{max} of Compounds **1a-c**

Compound	λ_{max}, nm				
	CCl_4	PhMe	AcOEt	MeCN	EtOH
1a	459, 557	459, 559	459, 559	462, 562	466, 567
1b	432, 657	426, 657	418, 663	419, 669	418, 674
1c	439, 522	442, 522	438, 520	438, 517	521

delocalization in the pyridinium betaine molecule. The UV-vis spectrum of compound **1b** differs from the spectra of compounds **1a** and **1c** not only in the position of the absorption bands (the absorption band I is weak and shows a negative solvatochromic effect), but by the intense positive solvatochromic effect of the absorption maximum II (+18 nm from PhMe to EtOH). The absorption bands of compound **1a** show a solvatochromic effect (+8 nm from PhMe to EtOH), but both absorption bands of compound **1c** do not exhibit solvent dependence. It can be concluded that incorporation of the cyano substituent in the pyridine unit of the betaine molecule caused substantial changes in the electronic structure of betaine **1b,** possibly due to the contribution of an additional important mesomeric structure:



The existence of two close negative charges in this structure also explains the observed tendency of betaine **1b** in solution and thermally to split off the indan-1,3-dione fragment.

Studies about the NLO properties of obtained chromophores are in progress.

EXPERIMENTAL

2-Dicyanomethylideneindane-1,3-dione oxide was obtained in accordance with [15]. All other starting materials were purchased from Acros. The purity of all compounds was checked by TLC on Merck

F_{254} silica plates. The spots were visualized when necessary in UV light and in iodine vapor. Chromatographic separations were carried out on silica gel (Merck, reinst) or Biotage SP1 HPLC using Biotage silica gel cartridges. Melting points were taken on an SMP 10 Stuart apparatus and ^{1}H NMR spectra were obtained on a Varian Mercury BB 200 MHz spectrometer against TMS as internal reference, and elemental analysis on a VARIO EL III CHNOS Elemental Analyzer. UV-vis spectra were recorded using a Lambda 35 Perkin–Elmer UV/VIS spectrometer. Waters Alliance 2695 HPLC was used with an XTerra® MS C18 column (2.1×100 mm, particle size 5 μm) and a Waters EMD 1000 MS detector; mass spectra were obtained in the ESI+ mode, cone voltage 30 V.

The properties of the main products are presented in Tables 1-5.

2,5-Dibromopyridine-4-amine (3). To a suspension of 4-aminopyridine (**2**) (4.7 g, 0.05 mol) N-bromosuccinimide (17.8 g, 0.1 mol) is added portionwise with intensive stirring. Stirring is continued at room temperature in the dark for 48 h, and then the solvent is evaporated under reduced pressure to obtain a mixture of succinimide, 4-amino-2-bromopyridine, and compound **2**. The mixture is extracted with 300 ml of CCl_4 in a Soxhlet extractor for 2 h. After evaporation of the CCl_4, a white precipitate (9.33 g) is obtained, which is recrystallized from 45 ml of EtOH. Yield 6.9 g (55%); mp 167-170°C [16]. Found, %: C 23.64; H 2.12; N 11.11. $C_5H_4Br_2N_2$. Calculated, %: C 23.80; H 1.58; N 11.11.

4-[N,N-Bis(2-hydroxyethyl)amino]-1-(3,5-dibromopyridin-4-ylazo)benzene (5a). Compound **3** (6 g, 0.024 mol) is added to a cooled mixture (-5°C) of H_3PO_4, 85% (19 ml) and HNO_3, 65% (13 ml). The mixture is stirred till complete dissolution (10 to 20 min) and cooled to -10°C. Isoamyl nitrite (3.3 ml, 0.024 mol) is added during 15 min and stirring continued for 45 min at -10°C to -5°C. The obtained solution is added dropwise with intensive stirring to the cooled solution of N,N-bis(2-hydroxyethyl)aminobenzene (4.5 g, 0.024 mol) in pyridine (40 ml). Simultaneously, ice (~80 g) is added in small pieces, and the temperature during addition is kept below 10°C. Stirring is continued for 1 h, and the temperature ia allowed to rise to room temperature. The precipitate is separated by filtration, washed with water, and dried. The crude product is boiled with EtOAc (20 ml), cooled, and the orange crystals filtered off. Yield 7.4 g. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.55 (8H, br.); 4.82 (2H, br.); 6.85 (2H, d, *J* = 9.1); 7.72 (2H, d, *J* = 9.1); 8.73 (2H, s).

4-[N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)amino]-1-(3,5-dibromopyridin-4-ylazo)benzene (5b). To a solution of compound **5a** (7.4 g, 0.016 mol) in 15 ml DMF 3,4-dihydro-2H-pyrane (5.2 ml, 0.048 mol) is added. The solution is stirred at 40 to 45°C for 24 h, diluted with water, and extracted with *tert*-butyl methyl ether. The organic layer is washed with water, dried over Na_2SO_4, and evaporated. The crude product is recrystallized from EtOH. Yield 8.5 g, light-red crystals.

4-[N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)amino]-1-(3-bromo-5-cyanopyridin-4-ylazo)-benzene (6a). To a solution of compound **5b** (4 g, 6.5 mmol) in 12 ml of DMF $Zn(CN)_2$ (0.78 g, 6.5 mmol) and 10 mg of CuCN are added under Ar. The mixture is stirred at 90°C for 1 h; after cooling, ice is added. The oily solid phase is separated by filtration below 5°C, then dissolved in the minimum amount of solvent mixture (diisopropyl ether–acetone, 3:1) and chromatographed on silica gel using the same solvent mixture as eluent. Two fractions are obtained – 1.2 g compound **6a** with R_f 0.73 as violet-black crystals, and 0.7 g compound **6b** with R_f 0.66. After evaporation of the solvent, both are recrystallized from EtOH.

4-[N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)amino]-1-(3,5-dicyanopyridin-4-ylazo)benzene (6b). CuCN (188 mg, 2.1 mmol) is added to a solution of compound **5b** (0.6, 1 mmol) in 4.5 ml DMSO, and the mixture is stirred at 95 to 100°C for 4 h under Ar. The reaction mixture is poured onto a mixture of 20 g ice and ethane-1,2-diamine (140 μl, 2.1 mmol), stirred, and filtered. The crude product is purified by silica gel chromatography with *tert*-butyl methyl ether as eluent. Yield 0.22 g, green crystals.

4-[N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)amino]-1-(3,5-diphenylpyridin-4-ylazo)benzene (6c). A mixture of compound **5b** (1g, 1.6 mmol), phenylboronic acid (0.6 g, 4.8 mmol), K_2CO_3 (1.6 g), H_2O (1.25 ml) and $Pd(PPh_3)_4$ (115 mg) in 10 ml of toluene is stirred and heated at 110°C under Ar for 4 h, cooled to room temperature, diluted with water, and extracted with toluene. The organic phase is dried (Na_2SO_4) and evaporated to yield a yellow oil. Compound **6c** is extracted from the oil with boiling hexane (200 ml) and purified by flash chromatography (hexane–*tert*-butyl methyl ether, 1:5).

4-[N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)amino]-1-(3-cyano-5-phenylpyridin-4-ylazo)-benzene (6d) is obtained from compound **6a** by an analogous procedure.

2-[4-N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)aminophenylazo-3,5-dibromopyridinium-1-yl]-1,3-dioxo-2,3-dihydro-1H-inden-2-ide (1a). Compound **7** (0.22 g, 1 mmol) is added portionwise to a solution of compound **5b** (0.61 g, 1 mmol) in 5 ml of MeCN at 80°C under Ar. The mixture is boiled for 4-5 h, cooled, and the precipitate is filtered off and recrystallized from MeCN. Yield 0.36 g, green crystals, purity 96% (by HPLC-MS). This product could be further purified by silica gel column chromatography with a mixture of dichloromethane–acetone, 20:1 as eluent. Mass spectrum (ESI+), *m/z*: 723.9 $[M+H]^+$, 726.0 $[M+H]^+$, 727.8 $[M+H]^+$, 580.0 $[M\text{-}Ind]^+$, 582.0 $[M\text{-}Ind]^+$, 583.9 $[M\text{-}Ind]^+$.

2-[4-N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)aminophenylazo-3-bromo-5-cyanopyridinium-1-yl]-1,3-dioxo-2,3-dihydro-1H-inden-2-ide (1b). A mixture of compound **1a** (0.48 g, 0.63 mmol), $Zn(CN)_2$ (40 mg, 0.34 mmol), and CuCN (3 mg) in 10 ml of DMF is heated at 90°C under Ar for 2 h, cooled, diluted with H_2O, and refrigerated overnight at 0-5°C. The crude product is filtered of, dissolved in a mixture of dichloromethane–acetone, 20:1, and purified by silica gel column chromatography with the same solvent mixture as eluent. The product (R_f 0.28) is washed with Et_2O to remove compound **6a**. Yield 0.2 g, green crystals with gold lustre. Mass spectrum (ESI+), *m/z*: 702.3 $[M+H]^+$, 704.2 $[M+H]^+$, 558.2 $[M\text{-}Ind]^+$, 560.2 $[M\text{-}Ind]^+$, 474.1 $[M\text{-}Ind\text{-}THP]^+$, 476.0 $[M\text{-}Ind\text{-}HP]^+$.

2-[4-N,N-Bis(2-(tetrahydro-2H-pyran-2-yloxyethyl)aminophenylazo-3,5-diphenylpyridinium-1-yl]-1,3-dioxo-2,3-dihydro-1H-inden-2-ide (1c). Compound **7** (0.33 g, 1.5 mmol) is added portionwise to a solution of compound **6c** (0.9 g, 1.5 mmol) in 18 ml of MeCN at 80°C under Ar. The mixture is boiled for 4-5 h, cooled, diluted with Et_2O, and refrigerated overnight at 0-5°C. The crude product is filtered off and purified by silica gel column chromatography with a mixture of dichloromethane–acetone, 10:1, as eluent. R_f 0.69. Yield 0.48 g, violet-brown crystals. Mass spectrum (ESI+), *m/z*: 751.5 $[M+H]^+$, 607.5 $[M\text{-}Ind]^+$.

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