

Supplementary Information

for

A New Class of Light-Fast Oxonol Dyes: Organic-Glass Forming Salts of Oxonol Anions and 4,4'-Bipyridinium Cations

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1. Materials

Meting points were uncorrected. Tetramethylsilane was used as an internal standard for NMR chemical shift and coupling constants are expressed in Hz.

1.1. Preparation of Oxonol Dyes

Tetramethylammonium 5-[5-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)-penta-1,3-dienyl]-2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-olate **2b**: A mixture of 1-aminonaphthalene (3.58 g, 25 mmol), *N,N'*-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride (5.6 g, 10 mmol), and 100 cm³ of ethanol was stirred under reflux for 12 h. The mixture was allowed to stand over night in a refrigerator. Water (100 cm³) was added and stirred vigorously. Resulting precipitates were collected by filtration, and dried to give *N,N'*-bis(1-naphthyl)-4,4'-bipyridinium dichloride (1.05 g, 21.8 %).

Aniline (1 cm³, 0.011 mol), *N,N'*-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride (2.8 g, 5.0 mmol), and 100 cm³ of *N,N*-dimethylformamide (DMF) were mixed and stirred for 10 h at 80 °C. Resulting precipitates were collected by filtration, rinsed with DMF, and dried to give *N,N'*-diphenyl-4,4'-bipyridinium dichloride (1.2 g, 63.5 %).

Triethyl amine (24.9 cm³, 0.18 mol) was added to a mixture of Meldrum's acid (17.2 g, 0.12 mol), 1,7-diphenyl-1,7-diazahepta-1,3,5-trien hydrochloride (14.2 g, 0.05 mol), and 100 cm³ of methanol. The mixture was stirred for 3 h at r.t., then Meldrum's acid (4.3 g, 0.03 mol) and triethylamine (4.2 cm³, 0.03 mol) was added and stirred for another 3 h. Insoluble part was filtered off and the solvent was removed from the filtrate. The residue was dissolved in dichloromethane and subjected to column chromatography (SiO₂, CH₂Cl₂/MeOH: 10/1). Removal of the solvent gave Triethylammonium 5-[5-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)-penta-1,3-dienyl]-2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-olate (CAS RN: 251984-73-3), **2a**, as a violet solid. *m/z* (MALDI) (+)102, (-)349; λ_{\max} (DMF)/nm: 558.3 (ϵ /dm³ mol⁻¹ cm⁻¹ 1.07 × 10⁵).

Tetramethylammonium bromide (0.15 g, 1.0 mmol), the oxonol dye **2a** (0.45 g, 1.0 mmol), and 10 cm³ of methanol were mixed, stirred and the solvent was removed under reduced pressure. Water (5 cm³) was added and the mixture was stirred for 3 h at r.t.

Precipitates were collected by filtration, rinsed with water, and dried to give the tetramethylammonium salt **2b** (0.3 g, 71 %). Mp 199.2–200 °C (dec); m/z (MALDI) (+)74, (–)349; λ_{\max} (DMF)/nm 558.3 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1.88×10^5); δ_{H} (400MHz, DMSO- d_6) 1.57 (12H, s), 3.14 (12H, s), 7.17 (2H, t, J 13.2), 7.53 (1H, t, J 12.8), 7.67 (2H, d, J 13.6); Found: C, 51.5; H, 7.4; N, 3.0. Calc. for $\text{C}_{21}\text{H}_{29}\text{NO}_8 \cdot 3.5\text{H}_2\text{O}$: C, 51.8; H, 7.5; N, 2.9 %.

N,N'-diphenyl-4,4'-bipyridinium bis{5-[5-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)-penta-1,3-dienyl]-2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-olate} **2c**: Triethylamine (33.7 cm³, 0.24 mol) was added to a mixture of Meldrum's acid (24.2 g, 0.17 mol), 1,7-diphenyl-1,7-diazahepta-1,3,5-trien hydrochloride (19.8 g, 0.07 mol) and 50 cm³ of methanol. The mixture was stirred for 3 h at r.t. Water (300 cm³) and conc. HCl (30 cm³) were added to the mixture. Resulting violet crystals were collected by filtration, rinsed with ethyl acetate, and dried to give the free oxonol dye, 5-[5-(6-hydroxy-2,2-dimethyl-4-oxo-4H-1,3-dioxin-5-yl)-2,4-pentadienylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (15.6 g, 63.6 %, CAS RN: 251984-72-2). *N,N'*-diphenyl-4,4'-bipyridinium dichloride (0.23 g, 0.6 mmol) was added to a solution of the free oxonol dye (0.35 g, 1.0 mmol) in 10 cm³ of methanol. Resulting precipitates were collected by filtration, rinsed with methanol, and dried to give oxonol salt, **2c**, as green powder almost quantitatively. Mp 201–202 °C (dec). m/z (MALDI) (+)310, (–)349. λ_{\max} (DMF)/nm 558.3 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1.83×10^5). δ_{H} (400MHz, DMSO- d_6) 1.56 (24H, s), 7.17 (4H, t, J 13), 7.53 (2H, t, J 12.8), 7.68 (4H, d, J 13.6), 7.82 (6H, br s), 7.98 (4H, br s), 9.05 (4H, br s), 9.70 (4H, br s). Found: C, 66.5; H, 5.1; N, 2.75. Calc. for $\text{C}_{56}\text{H}_{52}\text{N}_2\text{O}_{16}$: C, 66.7; H, 5.2; N, 2.8 %.

N,N'-di(1-naphthyl)-4,4'-bipyridinium bis{5-[5-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)-penta-1,3-dienyl]-2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-olate} **2d**: *N,N'*-dinaphthyl-4,4'-bipyridinium dichloride (0.24 g, 0.5 mmol) was added to a solution of the free oxonol dye (0.35 g, 1.0 mmol) in 10 cm³ of methanol and stirred for 3 h. Resulting precipitates were collected by filtration, rinsed with methanol, and dried to give oxonol salt **2d** (0.51 g, quant.) as green crystals. Mp 201.5–203 °C (dec); m/z (MALDI) (+)410, (–)349; λ_{\max} (DMF)/nm 558.3 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1.90×10^5); δ_{H} (400MHz, DMSO- d_6) 1.57 (24H, s), 7.18 (4H, t, J 13), 7.53 (2H, t, J 12.6), 7.55 (2H, s), 7.69 (4H, d, J 13.6), 7.8 (4H, m), 7.90 (2H, m), 8.14 (2H, br s), 8.30 (2H, d, J 8), 8.43 (2H, br d, J 7.6), 9.20 (4H, br s), 9.81 (4H, br s); Found: C, 68.0; H, 5.15; N, 2.5. Calcd for $\text{C}_{64}\text{H}_{56}\text{N}_2\text{O}_{16} \cdot \text{H}_2\text{O}$: C, 68.2; H, 5.2; N, 2.5 %.

N,N'-diphenyl-4,4'-bipyridinium 5-[7-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)hepta-1,3,5-trienyl]-2,2-dimethyl-6-oxo-6H-1,3-dioxin-4-olate **3b**:

Triethylamine (13.1 cm³, 43 mmol) was added to a mixture of Meldrum's acid (9.0g, 62mmol), 1,9-diphenyl-1,9-diazanona-1,3,5,7-tetraen hydrochloride (9.7g, 31mmol), and *N,N*-dimethylformamide (80 cm³). The mixture was stirred for 4 h at r.t. then CH₂Cl₂ (100 cm³) was added. The mixture was washed with water. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on SiO₂, eluted with CH₂Cl₂ then with CH₂Cl₂-MeOH gradually increasing the MeOH concentration. A blue fraction was collected and was again treated with column chromatography. The residue was treated with a mixture of ethyl acetate and hexane to give triethylammonium 5-[7-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-ylidene)-hepta-1,3,5-trienyl]-2,2-dimethyl-6-oxo-6*H*-1,3-dioxin-4-olate **3a** (3.4 g, 24 %) as blue powder. Mp 143.7–144.5 °C; λ_{\max} (*N*-methylpyrrolidone:NMP)/nm 664.2 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 1.92×10^5); m/z (MALDI) (+)102, (-)375; δ_{H} (300MHz, DMSO-*d*₆) 1.15 (9H, t, *J* 7), 1.57 (12H, s), 3.03(6H, bs), 6.29 (1H, t, *J* 13), 7.18 (2H, t, *J* 13), 7.32 (2H, t, *J* 13), 7.56 (2H, d, *J* 13).

N,N'-diphenyl-4,4'-bipyridinium dichloride (0.15 g, 0.39 mmol) to a methanol solution (10 cm³) of **3a** (0.25g, 0.66mmol). Resulting precipitates were collected by filtration and rinsed with methanol to give **3b** (0.26g, 74 %, CAS RN: 251984-70-0) as powdery solid with golden luster. Mp 178–179 °C (dec); λ_{\max} (NMP)/nm 664.5 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 2.381×10^5); m/z (MALDI) (+)310, (-)375; δ_{H} (400MHz, DMSO-*d*₆) 1.57 (24H, s), 6.29 (2H, t, *J* 12.4), 7.18 (4H, t, *J* 13.2), 7.32 (4H, t, *J* 12.8), 7.57 (4H, d, *J* 13.6), 7.82 (6H, br s), 7.97 (4H, br s), 9.06 (4H, br s), 9.70 (4H, br s).

1.2. Preparation of bis[*N,N*-diethyl-4-(1-ethyl-4,5-dicyanoimidazol-2-diazo)aniline-2-trifluoromethanesulfonylamidato]nickel(II) **4**

Ethyl iodide (5.32 cm³, 66.6 mmol), 3-acetamidoaniline (5.0 g, 33.3 mmol), sodium carbonate (17.6 g, 167 mmol) and *N,N*-dimethylacetamide (50 cm³) were mixed and stirred for 7 h at 80 °C with portion-wise addition of ethyl iodide (13.3 cm³, 167 mmol). The reaction mixture was poured into water, extracted with ethyl acetate. The organic layer was separated and the solvent was removed under reduced pressure to give 3-acetamido-*N,N*-diethylaniline (39.2 g, 57.1 %), which was used without further purification.

Ethanol (250 cm³) and conc. HCl (45 cm³) were added to 3-acetamido-*N,N*-diethylaniline (38 g, 184 mmol) and stirred under reflux for 7 h. After cooling to room temperature, the mixture was condensed under reduced pressure, poured into a saturated aqueous Na₂CO₃ solution, extracted with ethyl acetate. The solvent was removed under reduced pressure to give 3-(*N,N*-diethylamino)aniline

hydrochloride (30.5 g, 83 %), which was used without further purification.

To a mixture of 3-(*N,N*-diethylamino)aniline hydrochloride (30.5 g, 152 mmol) and 100 cm³ of acetic acid, trifluoromethanesulfonic anhydride (45.1g 160 mmol) was added drop wise. After a few minutes stirring, colorless crystals separated. The crystals were collected by filtration, rinsed with 100 cm³ of cold water, and dried to give 3-trifluoromethanesulfonamido-*N,N*-diethylaniline (38.6 g, 85.6 %), which was used without further purification.

2-amino-4,5-dicyanoimidazole (5.0 g, 37.6 mmol), ethyl iodide (5.9 g, 37 mmol), potassium carbonate (25.9 g, 188 mmol) and *N,N*-dimethylacetamide (40 cm³) were stirred for 30 min at r.t. Water (400 cm³) was added. The resulting solid material was collected by filtration and dried to give 2-amino-4,5-dicyano-1-ethylimidazole (21.7 g, 39.3 %), which was used without further purification.

To an ice-cooled solution of 2-amino-4,5-dicyano-1-ethylimidazole (1 g) in 12 cm³ of acetic acid and 8 cm³ of propionic acid, a cold solution of sodium nitrite (0.47 g) in 3.3 cm³ of conc. sulfuric acid was added drop wise. Resulting suspension was added drop wise to a solution of 3-trifluoromethanesulfonamido-*N,N*-diethylaniline (1.84 g) in 20 cm³ of methanol at r. t. After addition of an aqueous solution (50 cm³) of sodium acetate (10.1 g), the reaction mixture was extracted with ethyl acetate. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give 4,5-dicyano-1-ethyl-2-(4-*N,N*-diethylamino-2-trifluoromethanesulfonamidophenylazo)imidazole (0.65 g, 22 %, CAS RN:208340-09-4). Mp 149.5–151 °C; *m/z* (MALDI) (-)468 (M-H); λ_{\max} (MeOH)/nm 525.9 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.11×10^4); δ_{H} (300MHz, DMSO-*d*₆) 1.19 (6H, t, *J* 6.9), 1.45 (3H, t, *J* 7.2), 3.58 (4H, q, *J* 6.9), 4.49 (2H, q, *J* 7.2), 6.72 (1H, d, *J* 2.5), 6.87 (1H, dd, *J* 2.5 and 9.6), 7.84 (1H, d, *J* 9.6). (*cf.* Y. Kurose, Y. Okamoto, S. Maeda *Jpn. Pat.* (1998), *Kokai Tokkyo Koho* H10-204070).

To a methanol solution (50 cm³) of 4,5-dicyano-1-ethyl-2-(4-*N,N*-diethylamino-2-trifluoromethanesulfonamidatophenylazo)imidazole (3.5 g, 7.14 mmol), nickel(II) acetate tetrahydrate (2.13 g, 8.56 mmol) was added and the mixture was stirred for 2 h at r.t. Resulting purple precipitates were collected by filtration, rinsed with cold methanol and dried to give bis[*N,N*-diethyl-4-(1-ethyl-4,5-dicyanoimidazol-2-diazo)aniline-2-trifluoromethanesulfonylamidato]nickel(II), **4** (16.8 g, 45.6 %, CAS RN:208340-33-4), as powdery solid with a golden luster. Mp >300 °C; *m/z* (MALDI) 992 (M⁺); λ_{\max} (MeOH)/nm 572.4 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1.55×10^5). (*cf.* Y. Okamoto, Y. Kurose, S. Maeda, Y. Suzuki *Jpn. Pat.* (1999), *Kokai Tokkyo Koho* H11-166125). Purity

monitored with HPLC was 98.8 %.

2. Preparation and absorption spectra of dye films

General procedure: A dye film was prepared on a surface-hardened PMMA plate by spin coating (10 sec at 500 rpm then 20 sec at 1000 rpm) a dye solution (0.5 cm^3 , 20 mmol dm^{-3} in 2,2,3,3-tetrafluoro-1-propanol). The coated sample was irradiated with UV-filtered light from a 17000-lux Xe-lamp through the PMMA plate in an air-cooled merry-go-round apparatus with intermittent monitoring of the spectral change of absorption. The initial absorption spectra of the dye films are shown in Fig. 3.

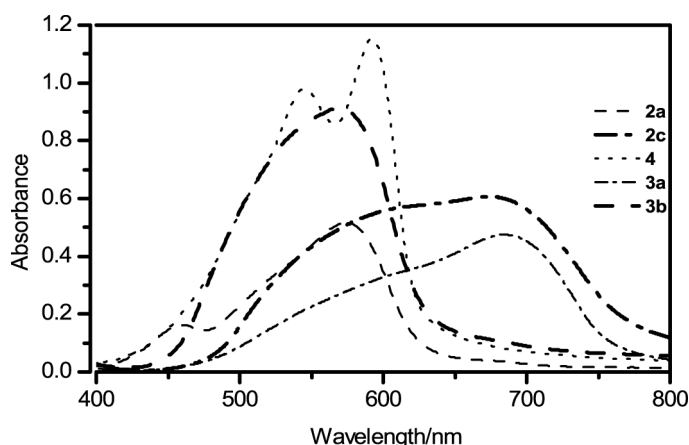


Fig. 3. Absorption spectra of dye films before irradiation.

3. Quenching Experiment

Fluorescence intensity was measured for chloroform solutions of **2b** ($5 \times 10^{-6} \text{ mol dm}^{-3}$) containing different amounts of *N,N'*-diphenyl-4,4'-bipyridinium dichloride **5**. The relative quantum yield of fluorescence was plotted against the concentration of **5** to give a straight line (Fig. 4B).

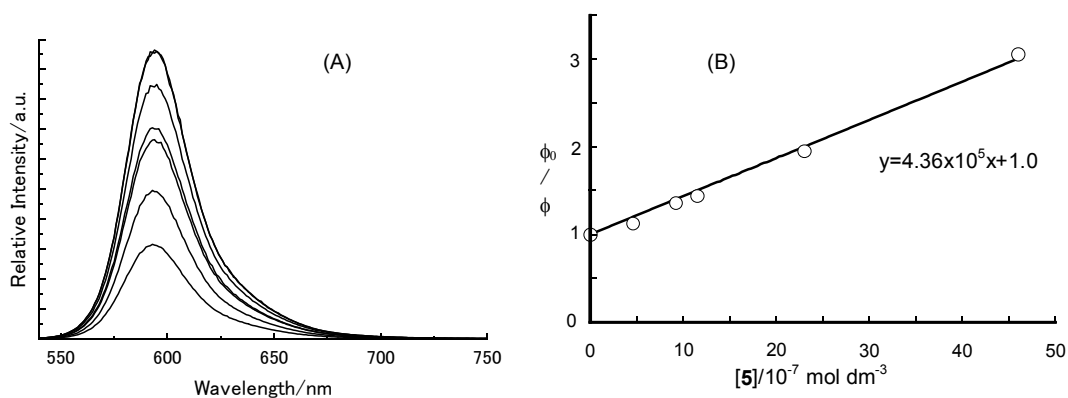


Fig. 4. (A) Decrease in fluorescence intensity of **2b** by addition of **5** in chloroform (containing 1 % methanol) and (B) a Stern-Volmer plot for fluorescence quenching.

Concentration of **2b** was 5×10^{-6} mol dm⁻³. Excitation wavelength is 530 nm.

4. Redox potential measurement

Redox potential measurements were carried out on a Yanaco polarographic analyzer P-1100. Reduction potential was measured with a dropping mercury working electrode, and oxidation potentials were measured with a rotating platinum working electrode. A saturated calomel electrode (SCE) was used as a reference electrode. The redox potentials of triethylammonium salts of oxonol dyes **2a** and **3a** were measured in DMF (1×10^{-3} mol dm⁻³) containing 0.1 mol dm⁻³ tetrapropylammonium perchlorate as supporting electrolyte. The reduction potential of *N,N*-diphenyl-4,4'-bipyridinium dichloride **5** was measured in a 1:1 (by volume) mixture of DMF (1×10^{-3} mol dm⁻³) and an aqueous NaH₂PO₄ solution (0.03 mol dm⁻³), the pH of which was adjusted to 3 with phosphoric acid.

Table 2. Redox potentials

Compounds	$E_{1/2}$ (Reduction) V vs SEC	$E_{1/2}$ (Oxidation) V vs SCE
5	-0.34, -0.55	
2a	-1.17	(0.5) ^{a)}
3a	-1.07	0.35

a) Reported for a salt with a cyanine cation in acetonitrile: A. S. Tatikolov, L. A. Shevedova, Kh. S. Dzhulibekov, Zh. A. Krasnaya, A. L. Sigantov, and V. A. Kuz'min, *Russ. Chem. Bull.*, 1995, **44**, 851.