

Supporting Information for:

Patterning Microparticles with Cationic Dye Nanoaggregates

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Eastman Kodak Company

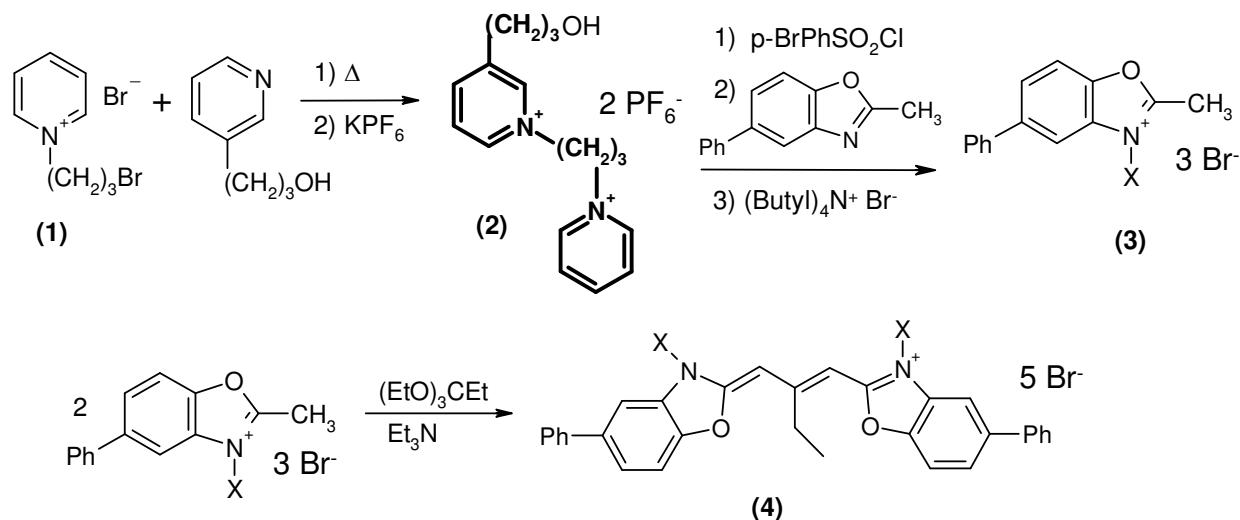
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1. Dye Synthesis

Scheme S1. Synthesis of Dye 4PYOxC3 (**4**)



Dye (**4**) Synthesis

Benzoxazolium, 5-phenyl-2-[2-[[5-phenyl-3-[3-[1-(3-pyridiniopropyl)pyridinium-3-yl]propyl]-2(3H)-benzoxazolylidene]methyl]-1-buten-1-yl]-3-[3-[1-(3-pyridiniopropyl)pyridinium-3-yl]-, bromide (1:5). To 40 mL of ethyl acetate were added 1,3-dibromopropane (40.0 g, 0.198 mol) and pyridine (3.92 g, 0.050 mol) and heated at reflux overnight, 13.0 g (93% yield) 1-(3-bromopropyl)pyridinium bromide, (**1**). To 200 mL acetonitrile was added (**1**) (13.0 g, 0.046 mol) and 3-pyridinepropanol (12.69 g, 0.093 mol), and heated to reflux overnight. After cooling, the solvent was decanted and the remaining brown oil dissolved in 70 mL of methanol and diluted with 200 mL water. This solution was slowly poured into 500 mL of potassium hexafluorophosphate (25.6 g, 0.139 mol) in water, stirred for 2 h, and the precipitate filtered, and rinsed sequentially with water, isopropanol, and hexane and dried, 11.60 g (46%) of a light beige solid, (**2**). The alcohol (**2**) (33.25 g, 0.061 mol) was dissolved in 300 mL of acetonitrile and cooled in an ice/acetone bath. Triethylamine (6.75 g, 0.067 mol) was added followed by bromobenzenesulfonyl chloride (17.04 g, 0.067 mol) portionwise. After stirring at 0 °C for 2 h the reaction was warmed to room temperature over 4-5 h and 250 mL of water added and stirred overnight. The mixture was poured into a solution of hexafluorophosphate (25.0 g) in 500 mL of water and stirred for 1 h. Water was added, precipitating the separated brown oil, trituration with IPA gave 34.0 g (73% yield) of the brosylate. The brosylate (34.0 g, 0.44 mol) and 2-methyl-5-phenylbenzoxazole (18.54 g, 0.089 mol) were suspended in acetonitrile (37 mL) and heated to 130 °C for 18 h. After cooling, the reaction mixture was diluted with ethyl acetate (100 mL), and decanted. Following a second dilution and decanting, the resultant

brown oil was dissolved in 250 mL of acetone and filtered into a stirred solution of tetrabutyl ammonium bromide (74.0 g, 0.228 mol) in 800 mL of acetone. The precipitated (3) was filtered under nitrogen, (very hygroscopic!). The product (3) was mixed with m-cresol (90 mL) heated to 75 °C, and triethyl orthopropionate (20 mL, 0.099 mol) was added followed by triethylamine (20.78 mL, 0.149 mol) at 80 °C. The reaction was kept at 100 °C for 3 h. The reaction mixture was cooled, and diluted into 1 L of acetone, and stirred for 2 h. The dye (4) was filtered, under nitrogen, rinsed with acetone and dried under nitrogen, affording a red solid (17.45 g, 26 % yield). The dye was taken up in a solvent mixture: 600 mL acetonitrile, 44 mL ethanol and 26 mL of methanol, and filtered hot into a solution of 11.0 g of tetrabutylammonium bromide in 400 mL of acetonitrile, and allowed to crystallize overnight.

2. Dye Analytical

Molar Absorptivity- In methanol; $\varepsilon = 1.82 \times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})$

NMR - ^1H NMR (500 MHz, CD_2Cl_2) δ : 9.65 (s, 2H); 9.50 (br, 4H); 9.22 (d, 2H, $J = 4.8 \text{ Hz}$); 8.58 (d, 2H, $J = 8.0 \text{ Hz}$); 8.44 (t, 2H, $J = 7.2 \text{ Hz}$); 8.04 (t, 4H, $J = 6.2 \text{ Hz}$); 7.92 (t, 2H, $J = 6.7 \text{ Hz}$); 7.70 (d, 4H, $J = 7.9 \text{ Hz}$); 7.65 (br, 2H); 7.58 (br, 4H); 7.50 (t, 4H, $J = 7.5 \text{ Hz}$); 7.42 (t, 2H, $J = 7.5 \text{ Hz}$); 5.10 (br, 10H); 4.50 (br, 4H); 3.35 (br, 6H); 3.05 (br, 4H); 2.40 (br, 4H); 1.42 (t, 3H, $J = 7.4 \text{ Hz}$).

LC/MS

$(\text{C}_{63}\text{H}_{61}\text{N}_6\text{O}_2)^+$, expected; 933.48505, observed; 933.48728

The HPLC instrument used was an Agilent (Santa Clara, CA, USA) 1100 series binary pump, autosampler, and diode array detector, with an Agilent Eclipse XDB C-8 HPLC column (50 x 2.1 mm, 5 μm). The mobile phases were A (0.01M ammonium acetate + 0.01M acetic acid buffer, pH 4.65 in HPLC-grade water) and B (1:1 v:v mixture of acetonitrile:2-propanol). A 10 min gradient from 10% B to 100% B was employed at a flow rate of 0.25 mL/min. The HPLC eluent was introduced directly into the source of the mass spectrometer. The singly charged species was detected at m/z 933.4873. The MS analysis was run with a PerSeptive Biosystems, Inc. (Framingham, MA., USA) Mariner Biospectrometry Workstation time of flight mass spectrometer operated in positive ion electrospray (Turbolon spray) mode. Data processing utilized the Applied Biosystems Data Explorer Version 4.0.0.1.

3. Polymer synthesis- In a 100 mL amber round bottom 1,2,3,4-tetrahydro-1,-naphthylideneamino *p*-styrenesulfonate (3.00 g, 0.0092 mol) and glycidyl methacrylate (Gm, 0.33 g, 0.0023 mol) were dissolved in THF (10.0 g, 15 % solids) and purged with nitrogen for about 30 min. Initiator, 2,2'-azobisisobutyronitrile, was added (0.06 g, 0.0003 mol, 3 mol % of combined monomers) and the flask sealed with a secured septum and set in a preheated oil bath at 65 °C for 8 h. The cooled solution was precipitated into ethyl acetate (300 mL). The

solid copolymer was filtered and re-dissolved in THF at 25% solids and precipitated into methanol (300 mL). The solid was collected by filtration and dried to yield 2.46 g (74 %). The polymer was dissolved in THF at 15% solids and 1,2,2,6,6-pentamethylpiperidine was added to provide storage stability. The resulting solution was stored in the refrigerator for up to 4 months before use.

4. Polymer Analytical.

Molecular Weight

Size-exclusion chromatography at 35.0 °C in N,N-dimethylformamide (DMF) containing 0.01 M lithium nitrate. The column set consisted of three Shodex KD-806M SDVB columns calibrated with narrow-molecular-weight distribution poly(methyl methacrylate) (PMMA) standards. Results reported in PMMA equivalents.

$M_n = 27.1K$ / $M_w = 104K$ / $M_z = 295K$.

NMR

1H NMR: The 1H NMR spectrum was obtained at 300 MHz. Approximately 10 mg was dissolved in 1 mL $CDCl_3$. TMS was added as a chemical shift reference.

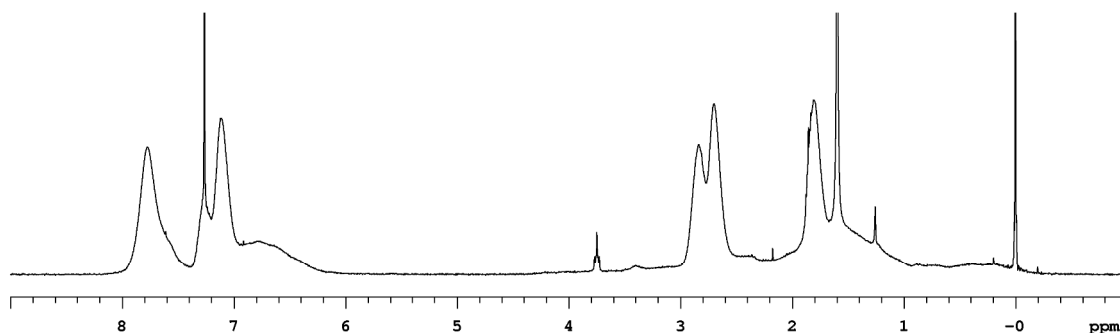


Figure S1 1H NMR Spectrum to TossGm8020

^{13}C NMR : Approximately 200 mg was dissolved in 3 mL CD_2Cl_2 . TMS was added as a chemical shift reference and $Cr(acac)_3$ as a relaxation agent. The ^{13}C NMR spectrum was obtained at 125 MHz. The composition, (mole percent), was determined from integral averages from several resonances of each monomer: Toss (86), Gm (14).

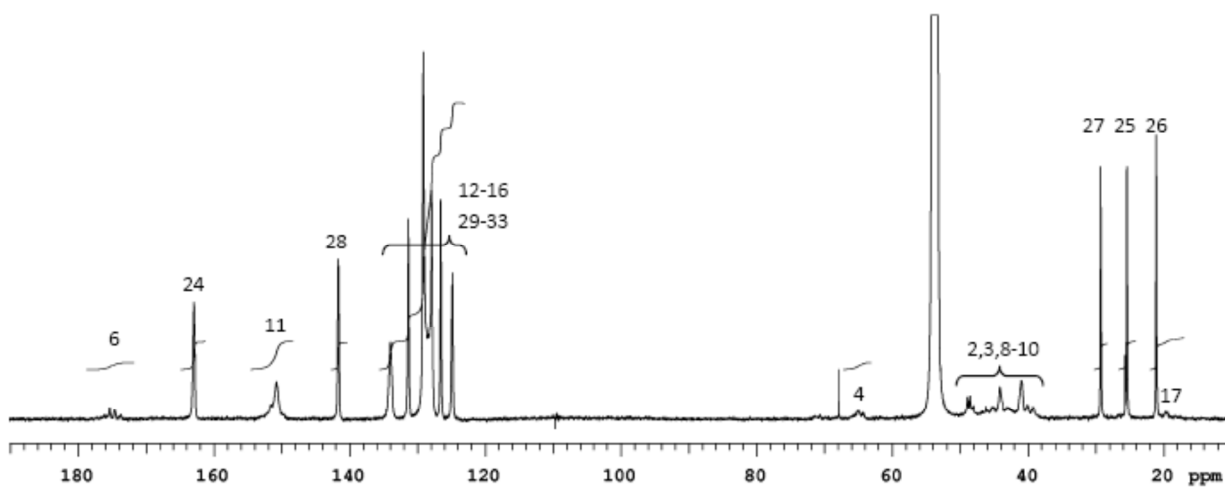


Figure S2 ¹³C NMR Spectrum of TossGm8020