

Electronic Supplementary Information (ESI) for

Spiropyran-based biodegradable polymer
all-optical transistors integrate the switching and
modulation of visible light frequency

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1. EXPERIMENTAL:

1(a). INSTRUMENTATION.

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated. isopropyl titanate, polymethylmethacrylate (PMMA) (Sigma-Aldrich, USA) were used as received without further purification. ϵ -Caprolactone (ϵ -CL) (Sigma-Aldrich, USA) was purified by drying over calcium hydride (CaH_2) and distilling under reduced pressure. calcium hydride, anhydrous ether, acetonitrile, dichloromethane, toluene, Dioxane, Tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd., China, and Dioxane, toluene and THF was dried using sodium wire and benzophenone as indicator. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. Reported yields are isolated yields. ¹HNMR spectra are reported in parts per million (PPM) relative to tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) indicates this particular copolymer to have a number average molecular weight (M_n) of 32900 with a polydispersity index (PDI) of 1.46. Monodisperse polystyrene standards were used to determine the M_n and PDI of the polymers from the GPC traces. Gel Permeation Chromatography (GPC) (PL50

apparatus equipped with two PLgel 5um MIXED-C columns, 300×7.5mm and one PL gel 5um Guard column, 50×7.5mm) at 40. Tetrahydrofuran was served as eluent at flow rate of 1.0mL/min. Polystyrene standard was used for calibration. H₂O (18.2 MΩ cm) was purified with a millipore Integral 3 system. The crystallinity of the SP-PCL polymer at room temperature was measured by X-ray diffraction (XRD) and Differential scanning calorimetry (DSC). DSC from -50 to 100°C at a heating rate of 10 °C/min under a nitrogen atmosphere. For XRD, The samples were placed in a quartz sample holder and scanned from 5 to 85° at a scanning rate of 5°/min.

UV-VIS: Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600)

PL: Edinburgh instruments (FLS 920 spectrometers)

¹HNMR: (Bruker AV400).

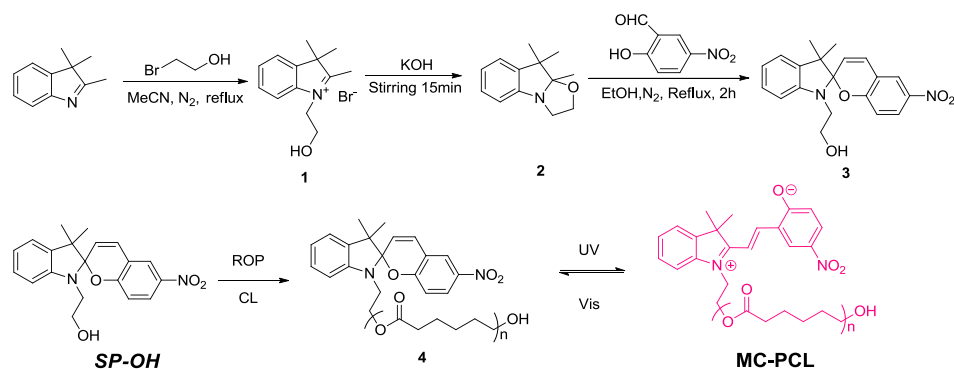
Mass Spectrometry: Agilent (1100 LC/MSD Trap).

GPC: varian, Inc. company PL-GPC 50.

DSC: PerkinElmer Instruments (Diamond DSC)

X-Ray Diffraction: PANalytical B.V. (X' Pert PRO).

1(b). SYNTHESIS PROCEDURES.



Scheme 1. Synthesis route to SP-OH monomer and SP-PCL polymers

2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol *SP-OH* (3).

The Compound 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol was prepared according to the previous literature¹ with slight modifications. The mixture of 2,3,3-trimethyl-3H-indole (16.06g, 100.86mmol), and 2-bromoethanol (13.23g, 105.87mmol) in acetonitrile (20ml) was heated to reflux for 24h under N₂. After cooling down to room temperature, the precipitation was filtered, washed with dichloromethane (DCM, 20ml × 3), collected and dried in the oven to afford 1 (26.33g, yield 91.87%) which was used in next step without purification. A solution of 1 (6.02g, 21.82mmol), KOH (2.78g, 49.64mmol) in distilled water (40ml) was stirred at room temperature for 30min, and then was extracted with Et₂O (3 × 30ml). The organic layer was collected, dried with Na₂SO₄ and concentrated under reduced pressure to afford 2 as yellow oil. To the oil, a solution of 5-nitrososalicylaldehyde (4.21g, 25.2mmol) in ethanol (40ml) was added and the mixture was heated for 3h under reflux and N₂. After cooling to room temperature, the precipitation was filtered, washed with ethanol and dried to afford *SP-OH* (3) as a purple solid (6.87g, yield 89.34%).

¹HNMR (400 MHz, CDCl₃): 1.21 (s, 3H), 1.31 (s, 3H), 3.32-3.38 (m, 1H), 3.44-3.51 (m, 1H), 3.71-3.85 (m, 2H), 5.88 (d, 1H, J = 10.4 Hz), 6.67 (d, 1H, J = 8.0 Hz), 6.76 (d, 1H, J = 8.8 Hz), 6.90 (m, 2H), 7.10 (d, 1H, J = 7.6 Hz), 7.19 (t, 1H), 8.00 (m, 2H).

MS m/z (APCI): [M+1]⁺ : 353.0

Preparation of SP initiators and SP-PCL polymers.

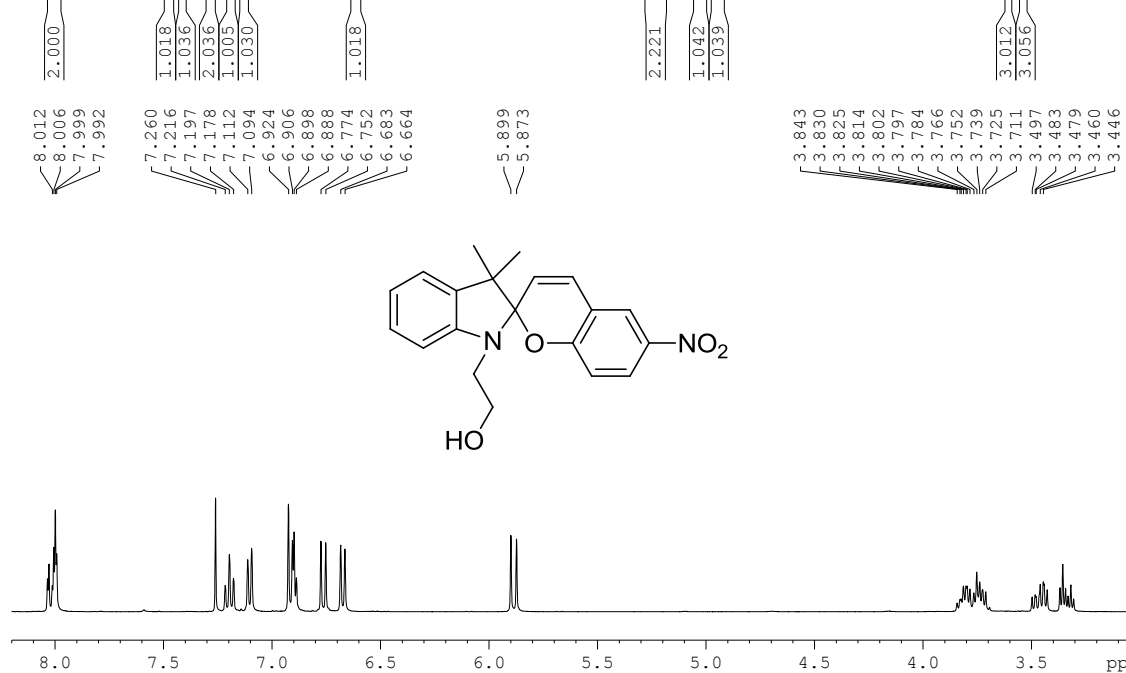
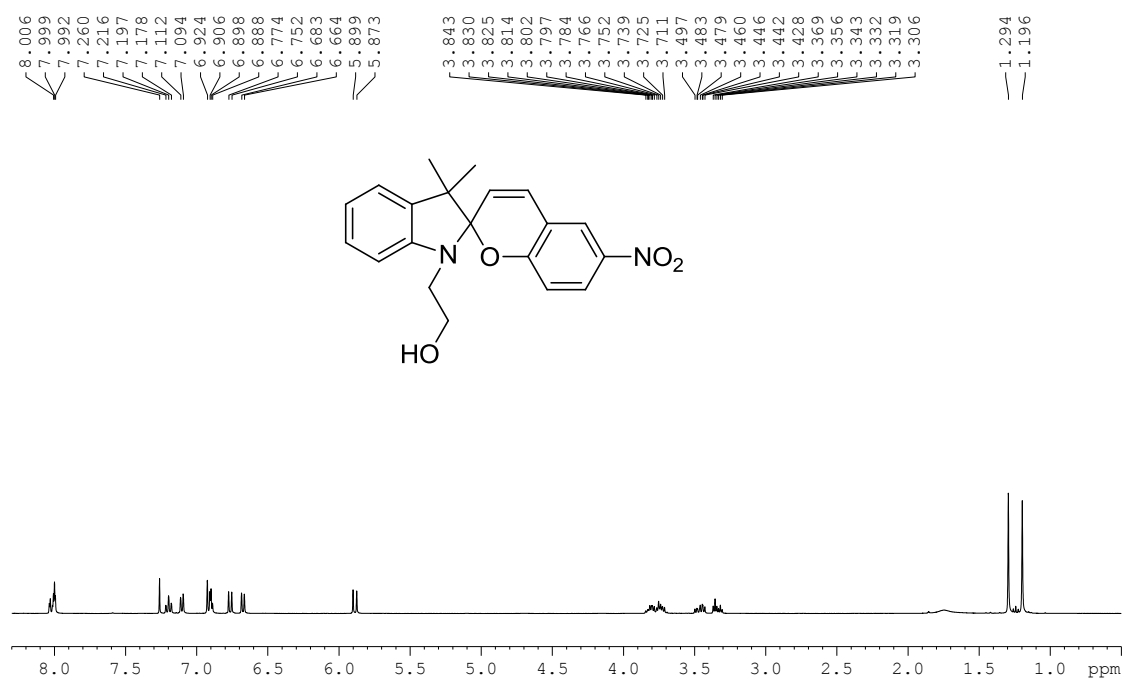
The SP-PCL polymers were prepared according to the previous literature² with slight modifications. Typically, A solution of SP-OH (18mg, 0.05mmol), isopropyl titanate (0.0125mmol) in toluene was heated at 60°C for 1h under N₂, and then the resulting solvent was slowly removed to obtain the SP initiators. Immediately, ε-caprolactone (2.2 ml, 20 mmol) was injected to the SP initiators *via* syringe. After the solution was heated and stirred for 10 h, the crude product was dissolved with chloroform and precipitated in anhydrous ether, and then dried in the oven overnight at room temperature. For ¹H NMR analysis, the SP-PCL with low molecular weight (SP-PCL 1) was synthesized. The ¹H NMR and GPC of the obtained SP-PCL polymers (SP-PCL 1 and SP-PCL 2) were provided.

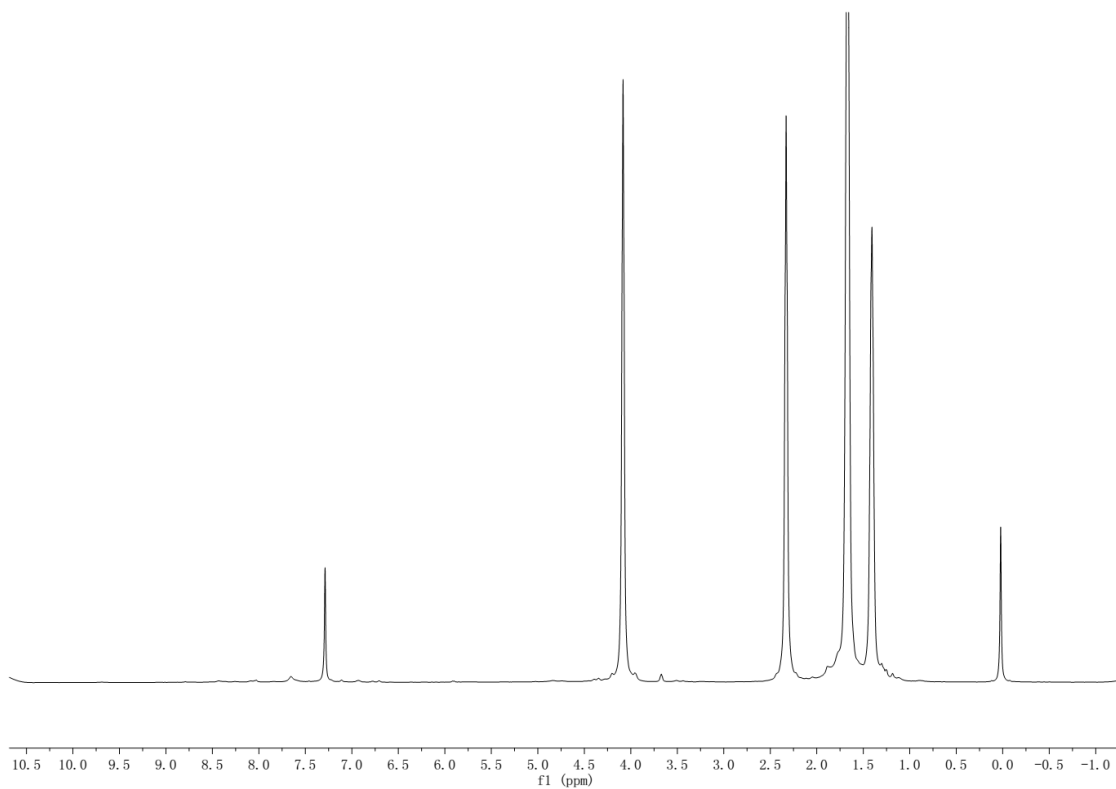
Preparation of SP samples for fluorescence measurement.

The solution absorption and emission spectra were acquired on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) and an Edinburgh fluorimeter (FLS 920 spectrometers) using a standard 1 cm path length quartz cuvette. For bulk spectra in polymer films, a small amount of highly concentrated SP-PCL (SP-PCL 2) solution was mixed into a PMMA solution (MW 75 000, atactic, polydispersity 2.8, Aldrich) in THF (SP-PCL:PMMA=1:9, w/w), then the solution was spin-cast onto a quartz slide producing a film 20 μm thick as measured by ellipsometry. Fluorescence quantum yields were referenced against standards with known quantum yields, corrected for differences in optical density and solvent refractive index. All quantitative measurements were done at low concentrations (absorbance values less than 0.1) to avoid any complications with dimer or aggregate formation.

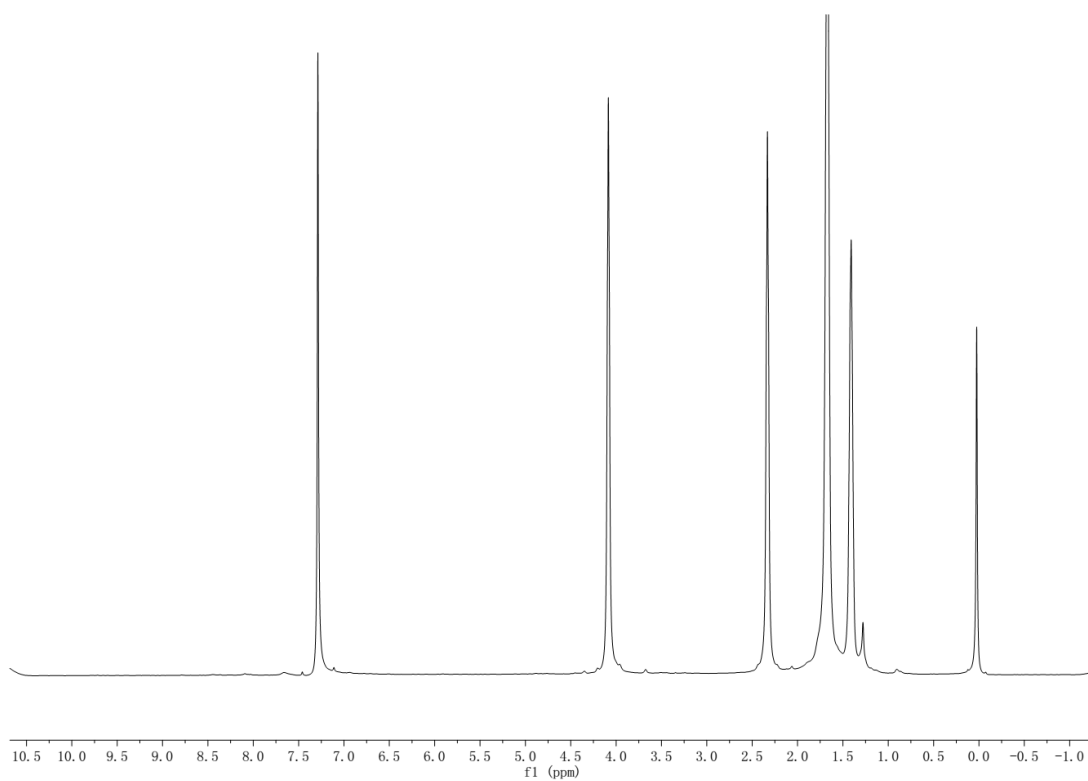
2. ¹HNMR spectra

2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol *SP-OH(3)*.



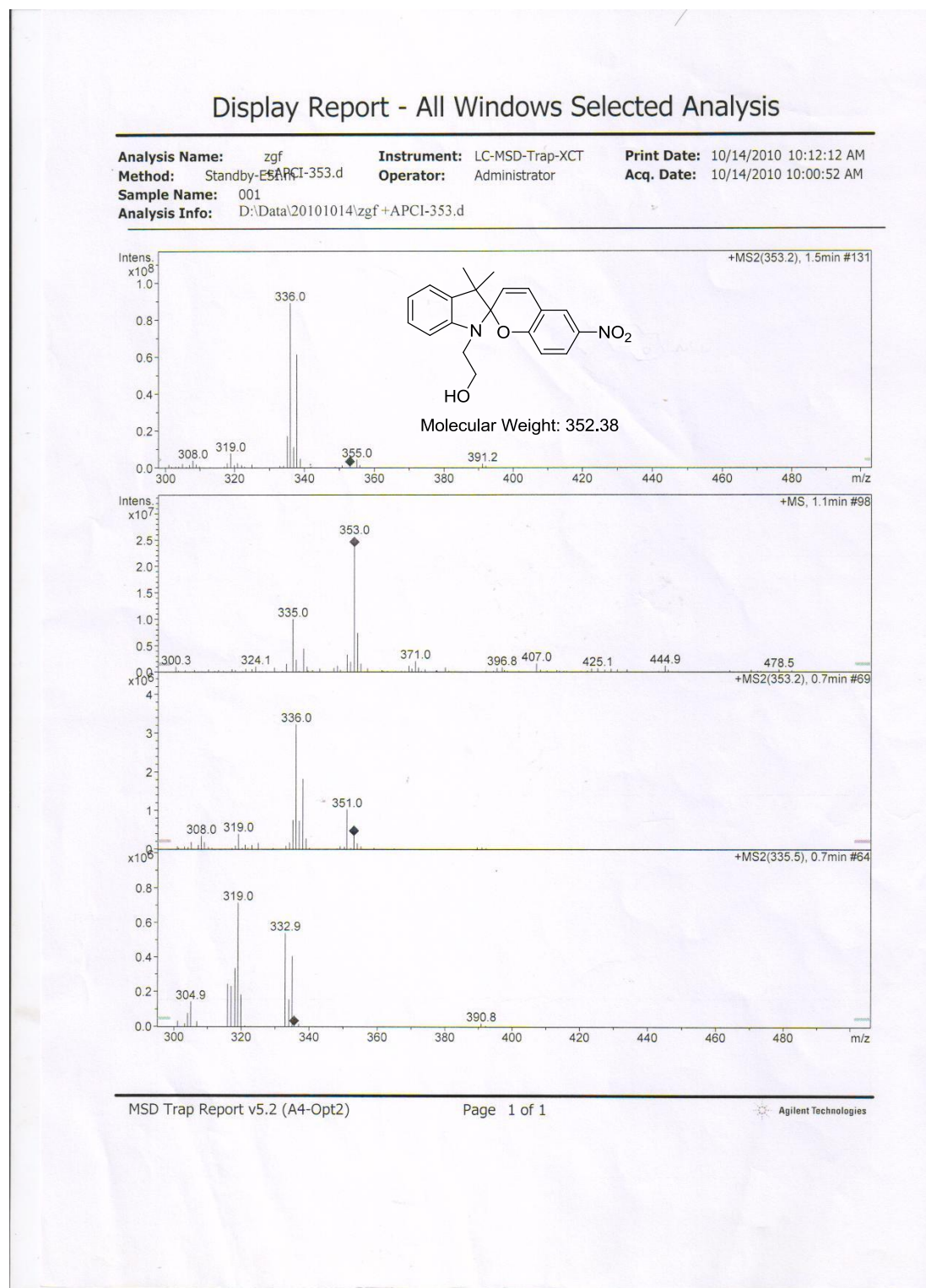


SP-PCL-1

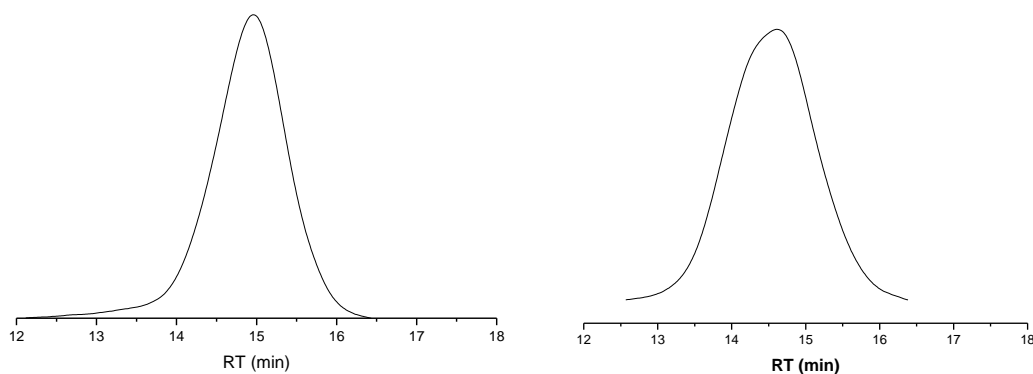


SP-PCL-2

3. Mass spectra



4. GPC profile of SP-PCL



SP-PCL-1 (MW = 22800, MWD = 1.36)

SP-PCL-2 (MW = 32900, MWD = 1.46)

5. Fluorescence quantum yield measurements

Table S1 Fluorescence quantum yields of SP-PCL and MC-PCL

Fluorophore	λ_{em} (nm)	QY in THF	QY in PMMA
SP-PCL	530	0.003	0.22
MC-PCL	650	0.006	0.36

^a for SP-PCL, relative fluorescence quantum yield in THF solution estimated using 9,10-diphenylanthracene ($\Phi = 0.90$ in cyclohexane⁴) as standard, relative fluorescence quantum yield in PMMA films estimated using 9,10-diphenylanthracene ($\Phi = 0.83$ in PMMA⁵) as standard, $\lambda_{ex} = 420$ nm.; for MC-PCL, relative fluorescence quantum yield in THF solution and in PMMA films estimated using Rhodamine B as standard^{6,7}, $\lambda_{ex} = 514$ nm.

6. References

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