Supporting Information

Stimulating changes in the elastic modulus of polymer materials by molecular photochromism

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Sample Preparation

The Ru-NB/NB copolymer was dissolved in cyclohexanone to obtain a solution concentration of 5% by weight. The solution was filtered by 0.2 µm size nylon syringe filter, followed by concentrated to approximately 20% by weight under vacuum line. A 0.5 mL of the solution was dropped onto a cover glass, which was cleaned by piranha solution, and rotated with a low speed at 800 rpm for 12 seconds and 1500 rpm for 60 seconds by a spincoater KW-4A from Chemat Technology. The obtained film was further rotated at 3000 rpm for 60 seconds, followed with annealing at 65 °C in the oven overnight, to get rid of any remaining solvent.

AFM Measurement

The AFM employed for all the measurements is MFP-3D-SA from Asylum Research. The probes used for normal surface topology scanning are Olympus AC160TS from Asylum Research, with a nominal spring constant of k=42 N/m and frequency of 300Hz. The probes utilized for nanoindentation were Diamond like carbon coated TESPD from Bruker, with a nominal spring constant of k=42 N/m and nominal pyramid tip shape and tip radius of ~15nm. The probes were used as received without any further treatment. The surface topology scanning was performed under tapping mode and nanoindentation is performed under contact mode in the air.

GPC of Polymers

Samples were prepared by dissolving ~20 mg of polymer to 10 mL dichloromethane in glass vials, for a final concentration of ~2 mg/mL. Vials were capped and swirled for approximately 5 minutes until thoroughly dissolved. Solutions were then filtered through a 0.45µm PTFE syringe filter (Whatman) directly into two pre-labeled 2mL screw-cap GC vials (Agilent) and capped. Vials containing non-irradiated authentic solutions were set aside while the second set of vials were individually irradiated using a blue laser pointer (UV, 405 nm, <5 mW intensity) for 5 minutes. All samples (irradiated and non-irradiated) were then loaded onto an Agilent 1100 GPC autosampler deck and GPC was performed using the conditions outlined below.

GPC Conditions

Eluent: THF+ 2 ppt $LiNO_3$

Columns: (2) PL 5µm Mixed D (7.5x300mm)

Temp: 35°C Injection Vol: 50µL

Flow Rate: 1.00mL/min

Sample Concentration: ~2 mg/mL

Detector: Viscotek dRI (35°C)

Calibration: Conventional GPC, standard column calibration using narrow Polystyrene (PS) standards from Agilent (EasiCAL2). All values reported as Polystyrene equivalent molecular weights.

Modeling/Analysis of Nanoindentation Data (Oliver-Pharr Model)

Penetrating the surface with an indenter tip with a loading force F_{max} on the tip, results in a penetration depth of h_{max}. When the tip reaches the maximum depth, the sample surface conformed to the tip shape at depth h_c, and this depth to the initial surface is h_s. During the unloading process, the tip has direct contact with the surface through h_t, and left unrecoverable depth h_f. The h_s could be given by:

$$h_s = \varepsilon \frac{F_{\max}}{S_{\max}} \qquad \text{Equation (1)}$$

where ε is a constant and S is elastic unloading stiffness. The ε depends on the geometry of the indenter, and a value of 0.75 was recommended for the pyramid indenter based on empirical observation. S is given by:

$$S = \frac{d_F}{d_h} \qquad \text{Equation (2)}$$

The unloading curve follows a power law, which is described by:

$$F = BE^*(h - h_f)^m \qquad \text{Equation (3)}$$

Where B and m are constants, BE^* and m could be deduced from the fitting of force vs displacement curve. The power constant m is related to the efficient indenter shape. For an ideal pyramid tip, the value of m is 1.5. But normally the actual value of m varies from 1.2~1.8. After the identification of Equation 3, S_{max} could be calculated by Equation 2.

The contact depth of the tip and the sample at maximum penetration depth is:

$$h_c = h_{\max} - h_s \qquad \text{Equation (4)}$$

By introducing Equation 1 into Equation 4, it turns into:

$$h_c = h_{\max} - \varepsilon \frac{F_{\max}}{S_{\max}} \qquad \text{Equation (5)}$$

The cross sectional area of the indenter and the surface is a function of the contact depth. For a pyramid indenter, the area function is:

$$A = 3\sqrt{3}\tan^2\theta \cdot h_c^2 \qquad \text{Equation (6)}$$

Once the contact area is determined, the hardness H and effective Young's modulus E^* is estimated by Equation 7 and Equation 8:

$$H = \frac{F_{\max}}{A} \qquad \text{Equation (7)}$$

$$E^* = \frac{1}{2\beta}\sqrt{\frac{\pi}{A}} \cdot S_{\max} \qquad \text{Equation (8)}$$

where β is taken as a dimensionless unity. The effective Young's modulus is a combination of the sample modulus and the tip modulus, it is defined by Equation 9:

$$\frac{1}{E^*} = \frac{1 - \upsilon_{\text{sample}}^2}{E_{\text{sample}}} + \frac{1 - \upsilon_{tip}^2}{E_{tip}} \qquad \text{Equation (9)}$$

where v is the Poisson ratio. The Poisson ratio could be measured for bulk materials, but it is relatively difficult in nanoscale. However, the Young's modulus of the tip is much larger than the sample. E_{tip} can be neglected, as it would just result in an error of less than 1%. In this work, the effective Young's modulus is used instead of the sample Young's modulus for abbreviation.

Table S1. The nanoindentation fitting result for poly-NB polymer film

No.	**E_c (MPa)**	**Stiffness (N/m)**	**Hardness (MPa)**	**Adhesion force(nN)**	**M**
1	129	48	81	70	2.3
2	126	45	95	105	2.8
3	150	59	79	98	2.8
4	145	55	88	91	2.4
5	157	64	74	108	2.4
6	132	49	92	104	2.3
7	145	58	77	119	2.2
8	142	58	71	41	1.9
9	126	44	100	97	2.2
10	122	39	123	63	2.2
11	116	41	98	57	2.1
12	135	45	110	57	2.1
13	150	57	87	76	1.8
14	137	49	96	70	2.1

No.1-7 are results before irradiated by 405nm laser light, No.8-14 are results after irradiated with 405nm laser light.

Table S2. The nanoindentation fitting result for poly-$[Ru(bpy)_2pySO\text{-}NB/NB]^{n+}$ 1:25 copolymer film

No	**E_c (MPa)**	**Stiffness(N/m)**	**Hardness (MPa)**	**Adhesion Force(nN)**	**M**
1	700	78	1059	287	1.4
2	684	80	951	260	1.4
3	679	80	941	259	1.5
4	681	80	937	220	1.5
5	678	78	984	273	1.4
6	682	77	1028	239	1.4
7	666	75	1014	261	1.4
8	665	77	969	255	1.4
9	671	77	996	271	1.4
10	667	78	952	256	1.4
11	681	81	934	288	1.4
12	692	83	916	258	1.4
13	716	82	991	252	1.4
14	711	81	1005	290	1.4

15	703	81	980	311	1.4
16	679	80	936	271	1.4
17	717	81	1024	313	1.4
18	705	82	968	311	1.4
19	712	80	1037	305	1.4
20	730	80	1085	254	1.4

No.1-10 are samples before irradiated by 405nm laser light, No.11-20 are samples after irradiated with 405nm laser light.

Table S3. The nanoindentation fitting result for poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 copolymer film

No	E_c (MPa)	Stiffness(N/m)	Hardness (MPa)	Adhesion Force(nN)	M
1	490	78	508	436	1.3
2	497	83	469	352	1.4
3	528	85	503	379	1.6
4	534	88	485	318	1.5
5	489	82	458	333	1.5
6	497	79	517	348	1.5
7	517	85	488	360	1.5
8	504	87	438	343	1.6
9	485	84	438	362	1.5
10	478	80	471	309	1.4
11	508	84	469	339	1.4

Table S3. Continued.

No	E_c (MPa)	Stiffness(N/m)	Hardness (MPa)	Adhesion Force(nN)	M
12	503	84	476	392	1.6
13	703	108	535	415	2.2
14	722	104	636	319	1.7
15	730	107	610	300	1.9
16	709	102	634	286	1.6
17	697	110	524	275	1.8
18	681	100	609	261	1.6
19	704	103	611	319	1.6
20	730	105	645	307	1.7
21	738	99	729	366	1.5
22	737	106	627	296	2.3
23	686	102	602	356	1.6
24	725	106	608	330	1.6

No.1-12 are results before irradiated by 405nm laser light, No.13-24 are results after irradiated with 405nm laser light.

Table S4. The nanoindentation fitting result for poly-RupySO-NB/NB 1:150 copolymer film

No	E_c (MPa)	Stiffness(N/m)	Hardness (MPa)	Adhesion Force(nN)	M
1	265	82	131	159	2.2
2	242	73	134	133	2.2
3	236	72	132	175	2.2
4	240	75	126	164	2.6
5	237	69	146	158	1.9
6	227	66	146	180	1.9
7	241	75	125	166	2.3
8	229	70	131	191	2.1
9	271	80	136	149	2.1
10	250	76	136	166	2.5
11	252	77	132	146	2.7
12	240	73	133	163	2.4
13	236	71	137	147	2.2
14	248	77	130	130	2.6
15	233	69	140	137	2.1
16	227	68	139	141	2.1

No.1-8 are results before irradiated by 405nm laser light, No.9-16 are results after irradiated with 405nm laser light.

Table S5. The nanoindentation fitting result for poly-RupyS-NB/NB 1:40 copolymer film

No	E_c (MPa)	Stiffness(N/m)	Hardness (MPa)	Adhesion Force(nN)	M
1	335	55	495	673	1.2
2	341	57	457	689	1.2
3	343	60	421	675	1.2
4	320	54	452	711	1.1
5	336	58	442	649	1.2
6	334	55	470	641	1.1
7	326	56	443	652	1.2
8	338	58	441	617	1.3
9	352	55	531	680	1.2
10	333	57	443	702	1.2
11	314	47	581	868	1.1
12	307	48	535	779	1.3
13	308	45	588	617	1.2
14	332	60	383	721	1.5
15	329	62	352	823	1.4

16	321	48	571	825	1.1
17	319	56	402	640	1.3
18	324	48	593	817	1.1
19	322	55	439	733	1.4
20	305	45	580	787	1.0

No.1-10 are results before irradiated by 405nm laser light, No.11-20 are results after irradiated by 405nm laser light.

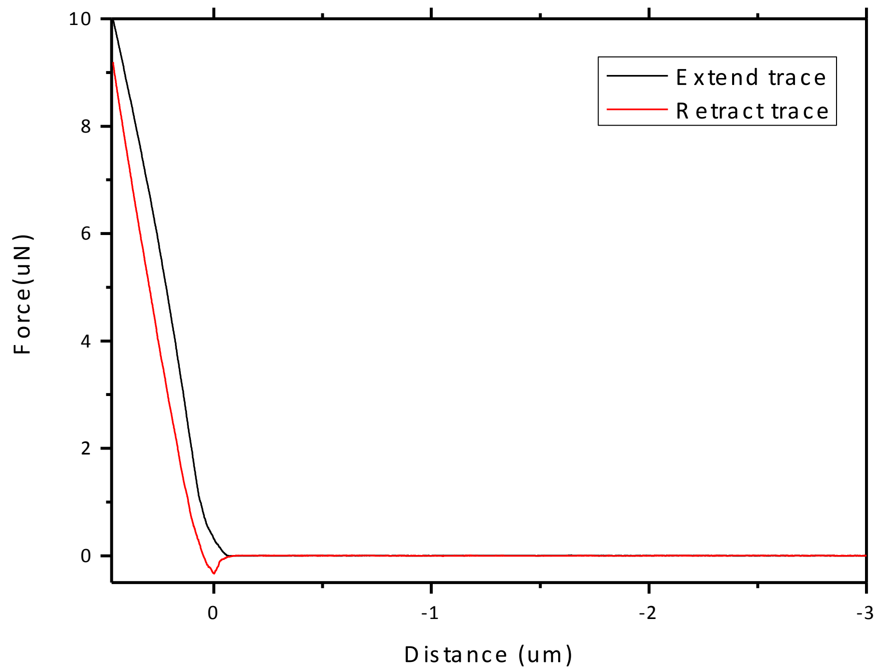

Figure S1. A typical force curve for poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 copolymer film. The black line represents the extend trace, where the probe is moving towards the surface; the red line represents the retract trace, where the probe is moving away the surface.

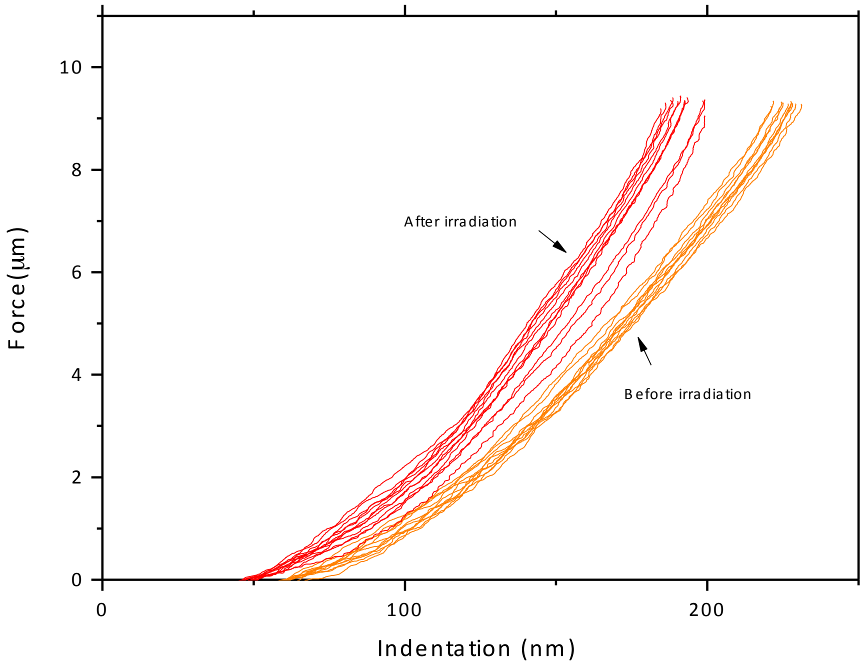

Figure S2. Force vs Indentation curve for poly-$[Ru(bpy)_2pySO\text{-}NB/NB]^{n+}$ 1:40 polymer film before and after irradiation with 405nm laser light. The solid red lines are the curves before irradiation, and the orange lines are the curves after irradiation.