

Supporting Information

Triple-diazonium reagent for virus crosslinking and the synthesis of an azo-linked molecular cage

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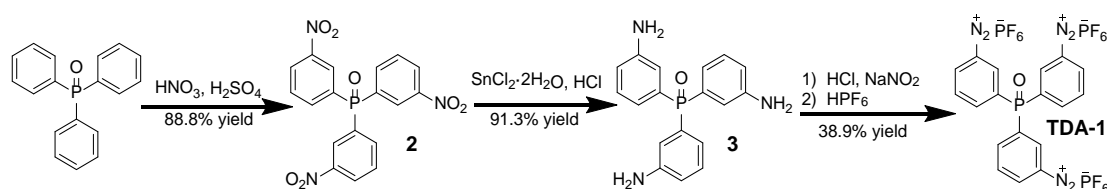
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1. Reagents and instruments

All chemicals and solvents used for synthesis were purchased from commercial suppliers and applied directly in the experiment without further purification. The progress of the reaction was monitored by TLC on pre-coated silica plates (Merck 60F-254, 250 μm in thickness), and spots were visualized by UV light. Merck silica gel 60 (70-200 mesh) was used for general column chromatography purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in parts per million relatives to internal standard tetramethylsilane ($\text{Si}(\text{CH}_3)_4 = 0.00$ ppm) or residual solvent peaks ($\text{CDCl}_3 = 7.26$ ppm, $\text{DMSO}-d_6 = 2.50$ ppm, $\text{MeOD} = 3.31$ ppm). ^1H NMR coupling constants (J) are reported in Hertz (Hz), and multiplicity is indicated as the following: s (singlet), d (doublet), m (multiplet), hept (heptet). High-resolution mass spectrum (HRMS) was obtained on an Agilent 6540 UHD Accurate-Mass Q-TOFLC/MS. The UV-visible spectra were recorded on a UV-6000 UV-VIS-NIR-spectrophotometer (METASH, China).

2. Synthesis



Synthesis of 2. Triphenylphosphine oxide (4.6 g, 16.5 mmol) dissolved in concentrated sulfuric acid (35 mL) was dropwise added to a mixed solution of concentrated H_2SO_4 (15 mL) and concentrated HNO_3 (15 mL) at 0°C . After stirring at room temperature for 6 hours, the reaction mixture was poured into ice-cooled H_2O (400 mL), and the precipitated yellow solid was collected by filtration. The resulted solid was recrystallized using EtOH to give the desired product as a pale yellow powdery solid (6.5 g, 89% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.57 – 8.46 (m, 6H), 8.25 – 8.18 (m, 3H), 7.95 – 7.89 (m, 3H).

Synthesis of 3. A mixture of compound **2** (3.34 g, 8.0 mmol) and stannous chloride dihydrate (18.02 g, 80.0 mmol) in 50 mL of EtOH and 25 mL of concentrated HCl was stirred at 40 °C for 6 hours until the reaction was completed, which was monitored by TLC (CH₂Cl₂ : MeOH = 5:1). The pH of the reaction solution was adjusted to 7-8 with 30% NaOH solution under an ice bath. Then, the filtrate was extracted with EtOAc, and the resulted organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH₂Cl₂: MeOH = 10:1) to obtain **3** (2.36 g, 91%). ¹H NMR (400 MHz, MeOD) δ 7.26 – 7.20 (m, 3H), 6.99 – 6.84 (m, 9H); ³¹P NMR (162 MHz, MeOD) δ 35.31.

Synthesis of triple-diazonium reagent TDA-1. Compound **3** (1.38g, 4.3mmol) was dissolved in 30 mL concentrated HCl and 15 mL H₂O. A water solution of NaNO₂ (1.79 g, 25.6 mmol) was slowly added to the **3** solution at 0-5 °C. After stirring for 1 hour, 5.5 mL of 60% HPF₆ was added to the mixture for stirring another 1 hour.¹ The product was collected by filtration and washed with ice-cold water, MeOH and CH₂Cl₂ to obtain a white solid **TDA-1** (1.32 g, 39% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.26 (d, *J* = 12.5 Hz, 3H), 8.99 (d, *J* = 8.3 Hz, 3H), 8.53 – 8.46 (m, 3H), 8.30 – 8.15 (m, 3H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 142.7, 137.0, 136.4, 132.5, 132.2, 118.5; ³¹P NMR (162 MHz, DMSO-*d*₆) δ 19.67, -144.21 (hept, *J*_{P-F} = 711.3 Hz). HRMS (ESI): *m/z* [M-PF₆]⁺ calculated for C₁₈H₁₂F₁₂N₆OP₃⁺: 649.0088; found: 649.0070.

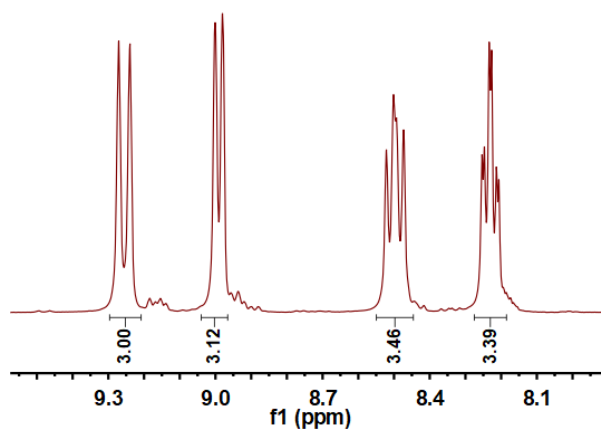
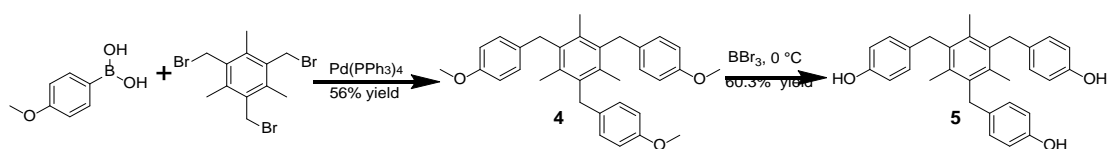


Fig. S1 Partial ¹H NMR (400 MHz, DMSO-*d*₆) spectrum of **TDA-1**. The high chemical shift values of aromatic H suggest the existence of positively charged substituents, and the integral values of the peaks imply that transformation of amine to diazonium moieties should be efficient.



Synthesis of 4.² 4-Methoxyphenylboronic acid (2.85 g, 18.8 mmol) and Na₂CO₃ aqueous solution (2 M, 23.5 mL) were added to a THF solution of 2,4,6-tribromomethyltrimethylbenzene (1.69 g, 4.23 mmol). The resulted mixture was degassed for 20 minutes, and the reaction flask was filled with argon, and then Pd(PPh₃)₄ (698 mg, 0.63 mmol, 15 mol%) was quickly added. After stirring for 24 hours, the reaction mixture was filtrated. The filtrate was extracted by EtOAc, and the resulted organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether : EtOAc = 100 : 6) to give compound **4** (1.138 g, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.95 (d, *J* = 8.7 Hz, 6H), 6.80 (d, *J* = 8.7 Hz, 6H), 4.08 (s, 6H), 3.78 (s, 9H), 2.15 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 157.8, 135.3, 134.7, 132.5, 128.9, 113.9, 55.4, 35.4, 16.8.

Synthesis of 5. BBr₃ (1.8 mL, 19.8 mmol) in 20 mL CH₂Cl₂ was slowly added to compound **4** (1.06 g, 2.2 mmol) in 20 mL CH₂Cl₂ at 0 °C under the protection of N₂. After stirring under N₂ for one day, MeOH (40 mL) was slowly added to the reaction mixture in an ice bath to quench the reaction. The solvent was removed under reduced pressure, and the residue was dissolved with EtOAc. The organic layer was washed with brine, dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. Finally, the crude product was purified by silica gel column chromatography (CH₂Cl₂ : MeOH = 100 : 3) to give a white solid **5** (582 mg, 60%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.11 (s, 3H), 6.77 (d, *J* = 8.4 Hz, 6H), 6.64 (d, *J* = 8.5 Hz, 6H), 3.94 (s, 6H), 2.06 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 135.1, 133.5, 130.0, 128.4, 115.2, 34.6, 16.3.

3. General procedures for spectroscopic studies

TDA-1 and 2,6-dimethylphenol (2,6-DMP) were dissolved in DMSO to prepare 1 mM and 100 mM stock solutions, respectively. UV spectra were measured in PBS (50

mM, pH 7.4, containing 5% DMSO) at 25 °C. All tests were carried out in a 3 mL quartz cuvette containing 2 mL of the tested solution.

For absorption spectrum tests: a mixture of 40 μL stock solution of **TDA-1** (final 20 μM) and 1954 μL PBS buffer was treated with 6 μL 2,6-DMP (final 300 μM). The resulted sample was monitored by UV-Vis spectroscopy at 220-600 nm with a certain time interval.

For kinetic tests: 20 μM **TDA-1** was mixed with different concentrations of 2,6-DMP (150, 200, 250, 300 μM) in 2 mL PBS buffer, respectively, and the time-dependent absorbance intensities at 360 nm were recorded. The pseudo-first-order rate constant, k_{obs} was determined by fitting the data with single exponential function. The linear fitting between k_{obs} and [2,6-DMP] gives the reaction rate constant k_2 .

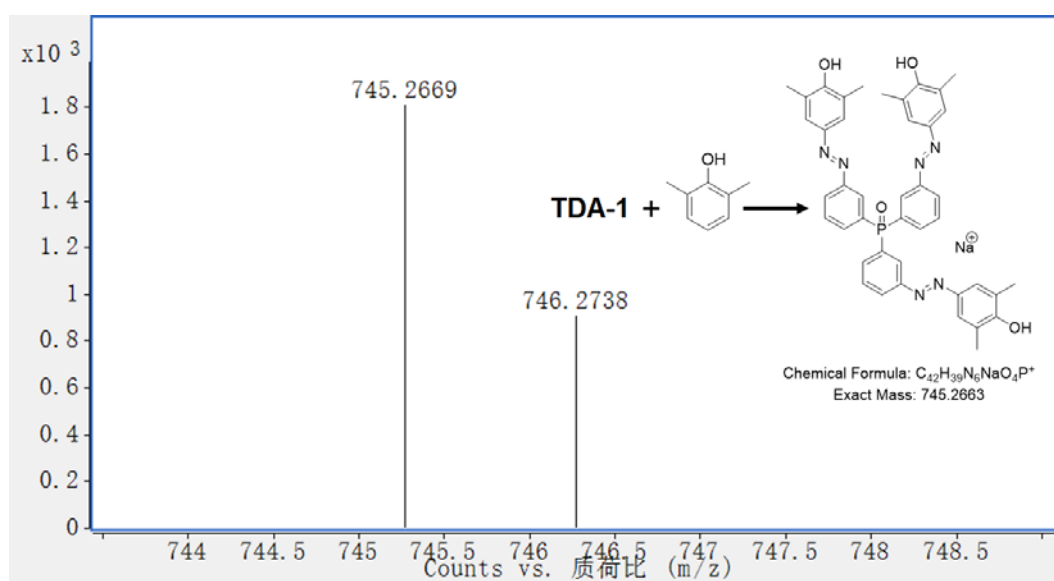


Fig. S2 HRMS analysis of the reaction aliquot of **TDA-1** (1 mM) incubated with 2,6-DMP (10 mM) in PBS buffer (50 mM, pH 7.4, containing 5% DMSO) for 2 hours. The m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{42}\text{H}_{39}\text{N}_6\text{O}_4\text{P}^+$: 745.2663, found: 745.2669.

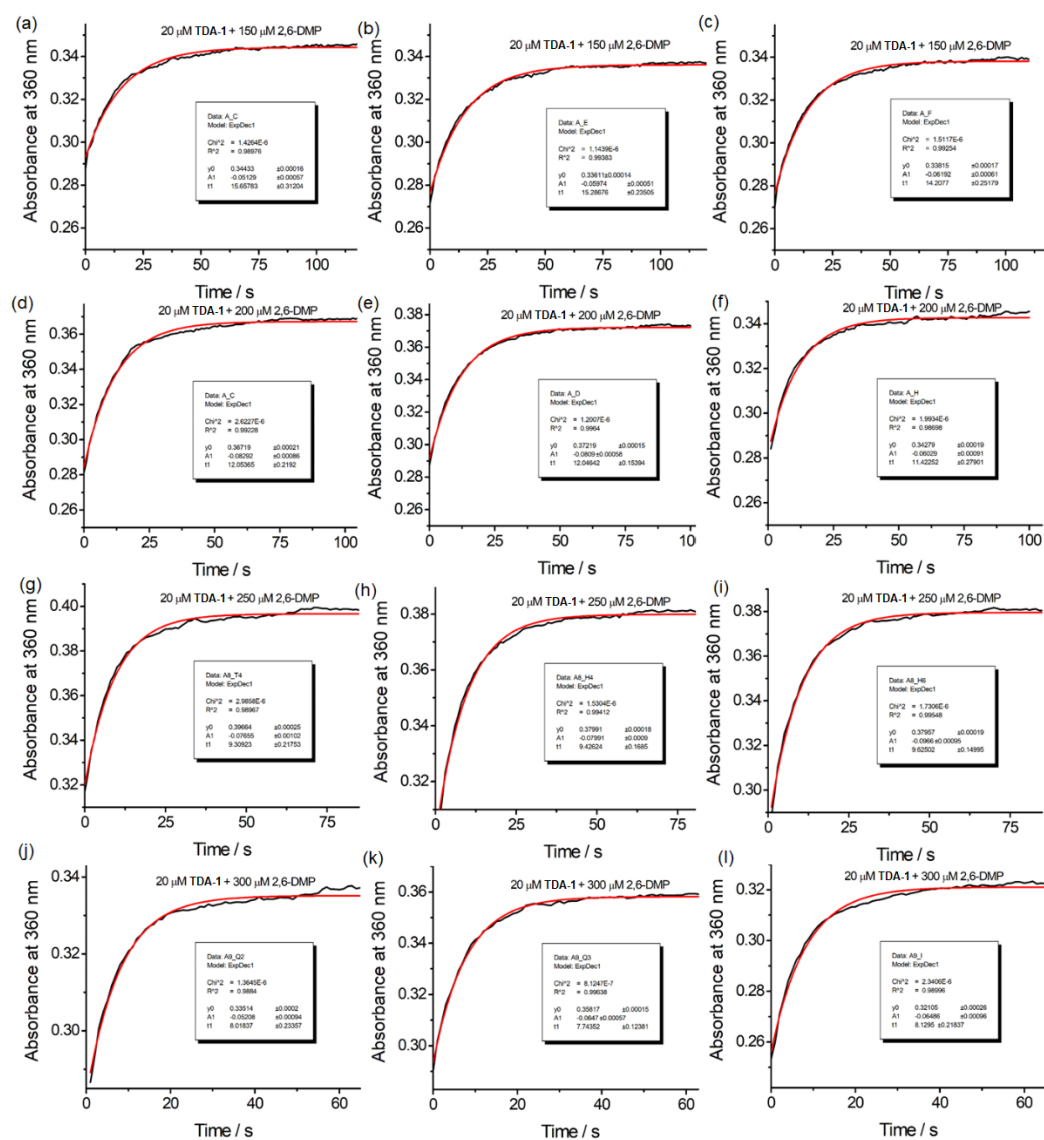


Fig. S3 Time-dependent UV-Vis absorbance intensities at 360 nm of **TDA-1** (20 μM) in the presence of different concentrations of 2,6-DMP (a-c. 150 μM ; d-f. 200 μM ; g-i. 250 μM ; j-l. 300 μM). The red lines represent the best fitting of the data to a single exponential function.

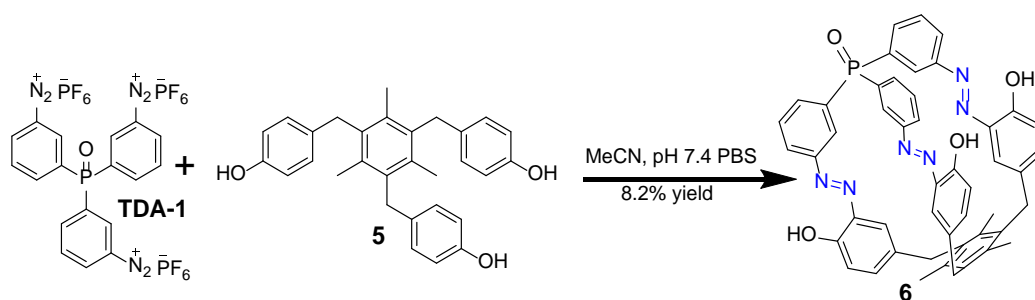
4. Construction of TMV-based hydrogel

TMV purification:³ TMV-inoculated tobacco leaves were ground fully and mixed with 25 mL phosphate buffer (0.2 mM, pH 7.0) including 250 μL β -mercaptoethanol (1%, v/v) on ice. After the filtration with two-layer screen cloth, the clear lysate was mixed with *N*-butyl alcohol (8%, v/v) for 15 min incubation. After centrifugation at 10,000 \times g for 20 min, the precipitate was dissolved again with 2 mL 0.01 M phosphate

buffer (pH 7.0) on ice and stirred for 6 h. After centrifugation, the pellet was resuspended in 5 mL 0.01 M phosphate buffer (pH 7.0) for 2 h. After centrifugation, the supernatant was then added with NaCl (4%, w/v) and PEG6000 (4%, w/v) for overnight precipitation. After centrifugation, the precipitate was resuspended in 2 mL 0.01 M phosphate buffer (pH 7.0) for 6 h. After centrifugation at 10,000×g for 5 min, the final virus suspension was obtained and the virus purity was evaluated according to the indicated ratio of A_{280}/A_{260} (0.84) and A_{260}/A_{248} (1.09). TMV concentration was calculated according to $C(\text{mg/mL}) = A_{260}/3.1$. TMV solution was stored at 4 °C for the following study.

With the TMV in hand, we constructed TMV-based hydrogel in PBS buffer (100 mM, pH 6.0) using triple-diazonium reagent **TDA-1**. First, **TDA-1** was dissolved in DMSO to prepare a 25-100 mM stock solution, and the concentration of TMV matrix was 2.5 mg/mL. TMV hydrogels were prepared by gently mixing TMV and different concentrations of **TDA-1** in glass vials at room temperature for 0-30 minutes to evaluate the gelation conditions. The gelation could be observed directly.

5. Synthesis and characterization of an azo-linked molecular cage



The coupling reaction between **TDA-1** and **5a** to form a molecular cage was unsuccessful after several attempts, which may be due to its unfavorable configuration (Fig. S4).

It is important to control the concentrations of **TDA-1** and **5** due to their multiple reactive sites. Firstly, we built an experiment device for the intramolecular coupling (Fig. S5). The coupling reaction could be carried out in neutral, weakly alkaline or

even weakly acidic solutions. We found the coupling reaction under pH 6.0 could lead to several unwanted species (Fig. S6). Finally, the optimized reaction was performed at pH 7.4, and the reactants were slowly mixed. The specific operations are as follows:

Compound **5** (95 mg, 0.22 mmol) was dissolved in 50 mL CH₃CN and 25 mL PBS buffer (50 mM, pH 7.4), and **TDA-1** (158 mg, 0.2 mmol) was dissolved in 50 mL CH₃CN and 25 g ice. At the same time, the both solutions were slowly dropped into a three-neck flask containing 100 mL CH₃CN under ice bath conditions, and the droplet rate was about 1 drop/s. After stirring for 1 hour, CH₃CN was removed under reduced pressure, and the water solution was extracted with EtOAc. After washing with saturated brine and drying with Na₂SO₄, the organic layer was concentrated under reduced pressure, and the resulted crude product was purified by silica gel column chromatography to obtain compound **6** (13 mg, 8.2%). ¹H NMR (400 MHz, CDCl₃) δ 12.54 (s, 3H), 8.41 – 8.33 (m, 3H), 7.85 (d, *J* = 7.8 Hz, 3H), 7.79 (d, *J* = 12.2 Hz, 3H), 7.75 – 7.68 (m, 3H), 7.45 – 7.40 (m, 3H), 7.36 (s, 3H), 7.04 (d, *J* = 8.5 Hz, 3H), 4.19 (s, 6H), 2.19 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.4, 150.9, 138.3, 135.8, 134.7, 134.5, 134.1, 133.5, 133.8, 131.9, 131. 130.3, 129.1, 118.8, 118.0, 35.5, 16.9; HRMS (ESI): *m/z* [M+H]⁺ calculated for C₄₈H₄₀F₁₂N₆O₄P⁺: 795.2843; found: 795.2843.

UV-vis spectrum of **6** was measured in H₂O at 25 °C. **6** was dissolved in DMSO to prepare a 0.5 mM stock solution. Then, 40 μL stock solution of **6** (final 10 μM) was added into 1960 μL H₂O.

HPLC analysis of **6** was tested using the DMSO solution. Conditions: ANGELA TECHNOLOGIES HPLC LC-10F; C18 column with 4.6 mm x 250 mm; detection wavelength: 318 nm. Buffer A: 0.1% (v/v) trifluoroacetic acid in water; buffer B: 0.1% (v/v) trifluoroacetic acid in MeOH; flow: 1 mL/min. The elution conditions were: 0-5 min, buffer B: 5-100%; 5-55 min, buffer B: 100-100%; 55-60 min, buffer B: 100-5%.

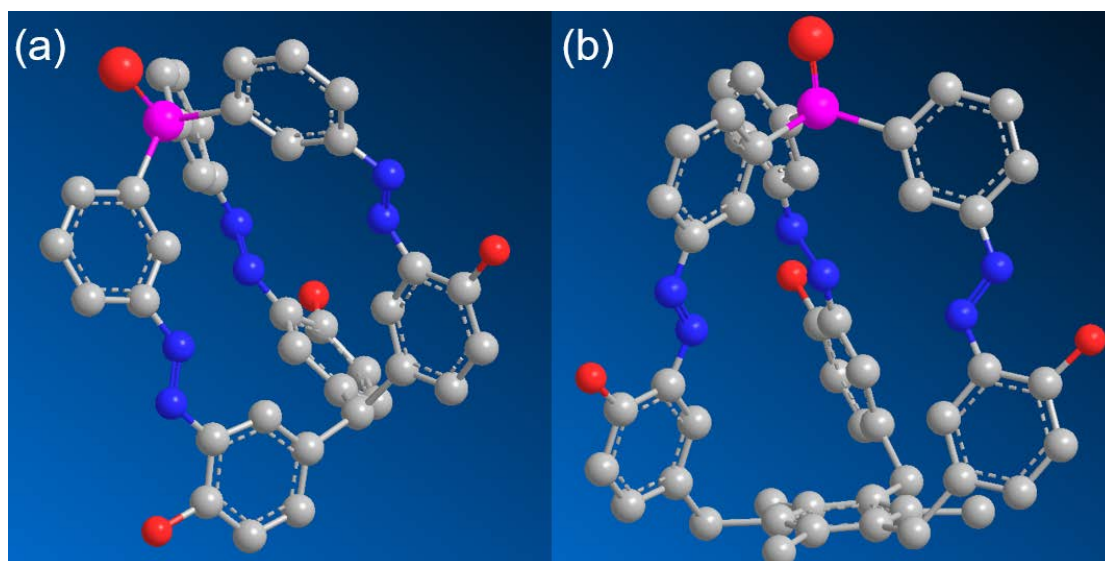


Fig. S4 ChemDraw 3D model structures (MM2 energy-minimized) of proposed CMCs based on 4,4',4''-methanetriyltriphenol **5a** (a) or **5** (b). The minimum energies were calculated as 135 kcal/mol and 69 kcal/mol for (a) and (b), respectively.

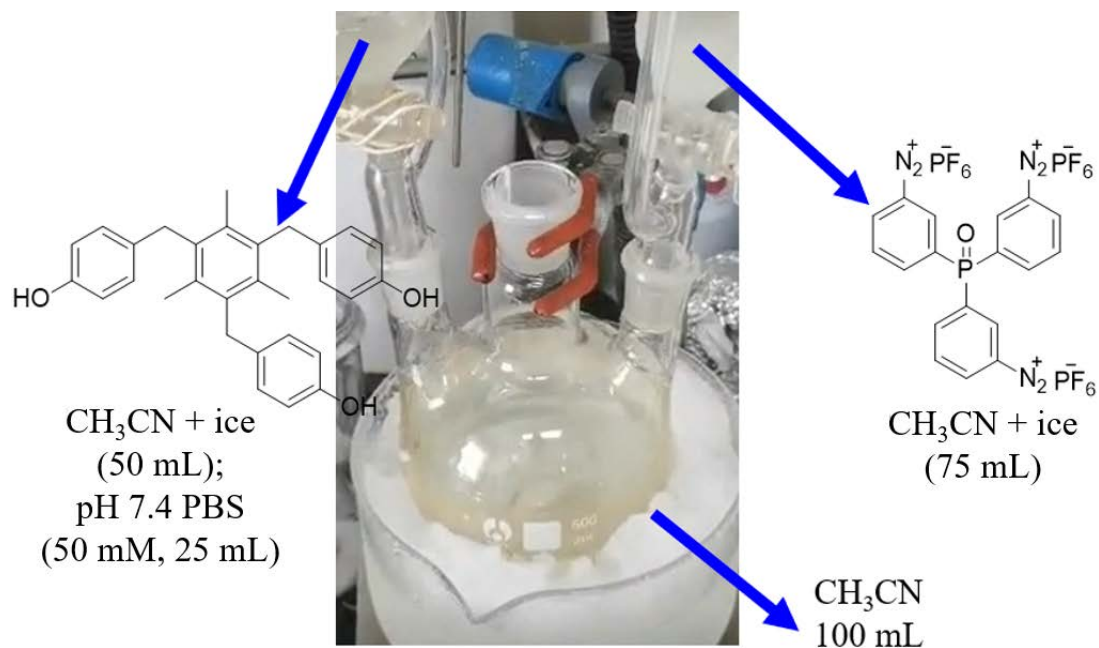


Fig. S5 Illustration of a low-concentration crosslinking device. 100 mL Acetonitrile was added to a three-neck flask under ice bath, and the two reactants in acetonitrile and ice water were added dropwise through a constant pressure dropping funnel at a rate of about 1 drop/s, respectively.

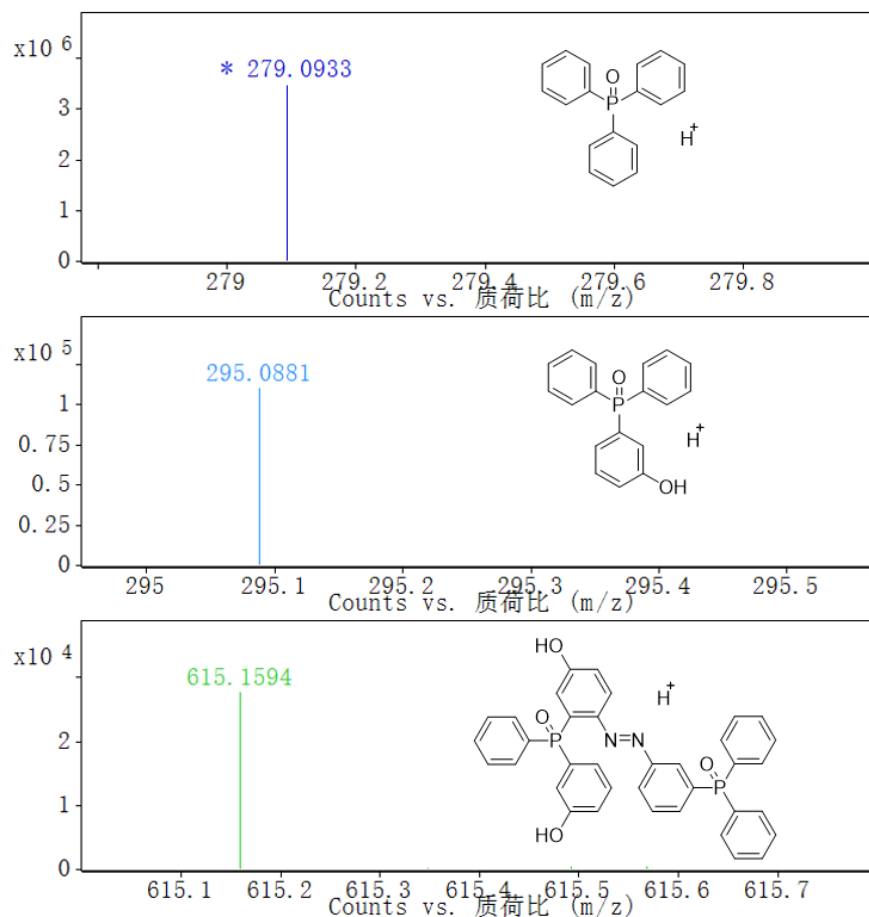


Fig. S6 HRMS analysis of the coupling reaction between **TDA-1** and **5** at pH 6.0. Under this condition, some by-products were suggested as inset.

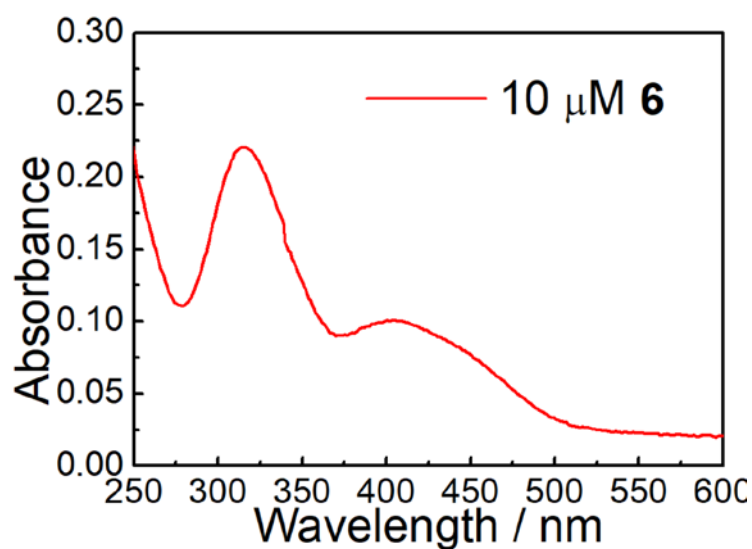


Fig. S7 The UV-vis absorbance spectrum of **6** ($10 \mu\text{M}$). The absorption peaks located at 315 nm and 405 nm should be due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the azo bond in **6**, respectively.

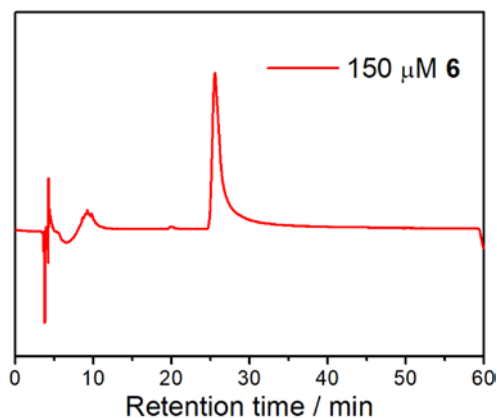


Fig. S8 HPLC trace of **6**. Detection wavelength: 318 nm.

6. X-ray crystallography studies of **6**

Crystals of **6** were obtained by recrystallization from chloroform and acetone (v:v, 1:3). The deep red single crystals were emerged after several days at 4 °C.

The single-crystal X-ray diffraction data set was collected on Gemin E diffractometer with Mo target. Used Olex2,⁴ and the structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97.⁵ Details of the data collection and the structure refinements are summarized in Table S1. Crystallographic data (CIF) file for the structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary (CCDC 2182065 for **6**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom, P: +44 (0)1223 336408, F: +44 (0)1223 336033 (e-mail: deposit@ccdc.cam.ac.uk).

Table S1 Crystal data and structure refinement for **6**

Empirical formula	C ₄₈ H ₃₉ N ₆ O ₄ P, 1.27979(CHCl ₃), 0.72021(C ₃ H ₆ O)
Formula weight	989.42
Temperature / K	112.6(5)
Crystal system	monoclinic
Space group	P2 ₁ /n
a / Å, b / Å, c / Å	12.7423(4), 15.4301(6), 25.1881(8)
α/°, β/°, γ/°	90.00, 99.673(3), 90.00
Volume / Å ³	4882.0(3)
Z	4

$\rho_{\text{calc}} / \text{mg mm}^{-3}$	1.346
μ / mm^{-1}	0.320
F(000)	2053
Crystal size / mm^3	$0.41 \times 0.35 \times 0.30$
2Θ range for data collection	6.2 to 52°
Index ranges	$-15 \leq h \leq 15, -19 \leq k \leq 14, -31 \leq l \leq 30$
Reflections collected	25542
Independent reflections	9364[R(int) = 0.0454 (inf-0.9Å)]
Data/restraints/parameters	9364/7/652
Goodness-of-fit on F^2	1.032
Final R indexes [$I > 2\sigma(I)$ i.e. $F_o > 4\sigma(F_o)$]	$R_1 = 0.0598, wR_2 = 0.1258$
Final R indexes [all data]	$R_1 = 0.0863, wR_2 = 0.1404$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.642/-0.631
Flack Parameters	N
Completeness	0.9969

Table S2 Bond length for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.4851(19)	C30	C56	1.385(4)
P1	C12	1.808(2)	C31	C53	1.394(3)
P1	C18	1.807(3)	C32	N41	1.413(4)
P1	C27	1.801(3)	C32	C50	1.406(4)
O4	C25	1.356(3)	C32	C51	1.408(4)
O3	C51	1.352(3)	C33	C44	1.394(4)
N10	C33	1.423(3)	C34	C40	1.407(4)
N10	N41	1.270(3)	C34	C54	1.522(4)
N11	N14	1.265(3)	C35	C53	1.381(4)
N11	C21	1.417(3)	C36	C37	1.381(4)
C12	C31	1.392(3)	C36	C46	1.399(4)
C12	C39	1.393(3)	C38	C64	1.514(4)
N14	C17	1.431(3)	C40	C63	1.377(4)
N15	N16	1.266(3)	C42	C63	1.396(4)
N15	C22	1.417(3)	C43	C46	1.380(4)
N16	C47	1.432(3)	C45	C57	1.399(4)
C17	C35	1.390(4)	C45	C59	1.375(4)
C17	C39	1.391(3)	C46	C52	1.512(4)
C18	C20	1.391(4)	C47	C58	1.382(4)
C18	C29	1.396(4)	C48	C58	1.383(4)
O2	C42	1.348(3)	C49	C56	1.380(4)
C20	C47	1.391(4)	C50	C57	1.382(4)
C21	C25	1.398(4)	C51	C59	1.389(4)
C21	C43	1.402(4)	C55	C62	1.509(4)
C22	C23	1.406(4)	C55	C65	1.414(4)
C22	C42	1.404(4)	C57	C61	1.522(4)
C23	C34	1.380(4)	C61	C65	1.512(4)
C24	C26	1.397(4)	C12	C69	1.761(5)
C24	C38	1.403(4)	C13	C69	1.759(5)
C24	C52	1.522(4)	C15	C69	1.737(5)
C25	C37	1.399(4)	C14	C66	1.743(6)
C26	C60	1.522(4)	C18	C66	1.712(6)

C26	C65	1.403(4)	C113	C66	1.751(6)
C27	C44	1.394(4)	O0AA	C102	1.151(14)
C27	C49	1.405(3)	C101	C102	1.538(14)
C28	C38	1.404(4)	O1AA	C105	1.180(16)
C28	C54	1.521(4)	C103	C102	1.492(14)
C28	C55	1.398(4)	C104	C105	1.500(16)
C29	C48	1.388(4)	C105	C106	1.523(17)
C30	C33	1.393(4)			

Table S3 Bond angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	C12	112.10(12)	C37	C36	C46	122.0(2)
O1	P1	C18	111.64(12)	C36	C37	C25	120.1(3)
O1	P1	C27	112.24(11)	C24	C38	C28	119.8(3)
C18	P1	C12	107.88(11)	C24	C38	C64	119.4(3)
C27	P1	C12	105.97(12)	C28	C38	C64	120.8(3)
C27	P1	C18	106.66(12)	C17	C39	C12	119.8(2)
N41	N10	C33	115.0(2)	C63	C40	C34	121.7(3)
N14	N11	C21	114.3(2)	N10	N41	C32	114.4(2)
C31	C12	P1	116.61(18)	O2	C42	C22	123.2(3)
C31	C12	C39	119.5(2)	O2	C42	C63	117.9(2)
C39	C12	P1	123.9(2)	C63	C42	C22	118.9(3)
N11	N14	C17	112.3(2)	C46	C43	C21	121.2(3)
N16	N15	C22	114.6(2)	C33	C44	C27	119.8(2)
N15	N16	C47	114.6(2)	C59	C45	C57	122.0(3)
C35	C17	N14	123.1(2)	C36	C46	C52	118.6(2)
C35	C17	C39	120.7(2)	C43	C46	C36	117.7(3)
C39	C17	N14	116.1(2)	C43	C46	C52	123.4(3)
C20	C18	P1	123.3(2)	C20	C47	N16	122.6(2)
C20	C18	C29	119.7(2)	C58	C47	N16	116.7(2)
C29	C18	P1	117.0(2)	C58	C47	C20	120.6(3)
C47	C20	C18	119.5(3)	C58	C48	C29	120.0(3)
C25	C21	N11	115.6(2)	C56	C49	C27	119.9(3)
C25	C21	C43	120.3(2)	C57	C50	C32	121.4(3)
C43	C21	N11	123.8(2)	O3	C51	C32	122.6(3)
C23	C22	N15	115.5(2)	O3	C51	C59	118.6(3)
C42	C22	N15	124.8(2)	C59	C51	C32	118.8(3)
C42	C22	C23	119.6(3)	C46	C52	C24	118.7(2)
C34	C23	C22	121.5(2)	C35	C53	C31	120.6(2)
C26	C24	C38	120.0(3)	C28	C54	C34	115.5(2)
C26	C24	C52	120.4(2)	C28	C55	C62	119.9(3)
C38	C24	C52	119.4(3)	C28	C55	C65	119.5(3)
O4	C25	C21	124.7(2)	C65	C55	C62	120.5(3)
O4	C25	C37	116.8(2)	C49	C56	C30	120.7(3)
C21	C25	C37	118.5(3)	C45	C57	C61	118.9(3)
C24	C26	C60	119.8(3)	C50	C57	C45	117.7(3)
C24	C26	C65	120.0(2)	C50	C57	C61	123.3(3)
C65	C26	C60	120.1(3)	C47	C58	C48	120.0(3)
C44	C27	P1	122.40(19)	C45	C59	C51	120.5(3)
C44	C27	C49	119.7(3)	C65	C61	C57	118.0(2)
C49	C27	P1	117.9(2)	C40	C63	C42	120.3(3)
C38	C28	C54	119.8(3)	C26	C65	C55	119.9(3)
C55	C28	C38	120.4(3)	C26	C65	C61	120.7(3)
C55	C28	C54	119.7(3)	C55	C65	C61	119.2(3)
C48	C29	C18	120.1(3)	C13	C69	C12	108.2(3)

C56	C30	C33	119.8(3)	C15	C69	C12	111.7(3)
C12	C31	C53	120.0(2)	C15	C69	C13	111.7(3)
C50	C32	N41	115.5(3)	C14	C66	C113	109.5(3)
C50	C32	C51	119.5(3)	C18	C66	C14	110.7(3)
C51	C32	N41	125.0(2)	C18	C66	C113	111.5(4)
C30	C33	N10	116.5(3)	O0AA	C102	C101	124.3(13)
C30	C33	C44	120.2(3)	O0AA	C102	C103	122.4(13)
C44	C33	N10	123.2(2)	C103	C102	C101	113.0(14)
C23	C34	C40	117.8(2)	O1AA	C105	C104	130.9(18)
C23	C34	C54	123.5(2)	O1AA	C105	C106	128.6(17)
C40	C34	C54	118.7(2)	C104	C105	C106	99.9(16)
C53	C35	C17	119.3(2)				

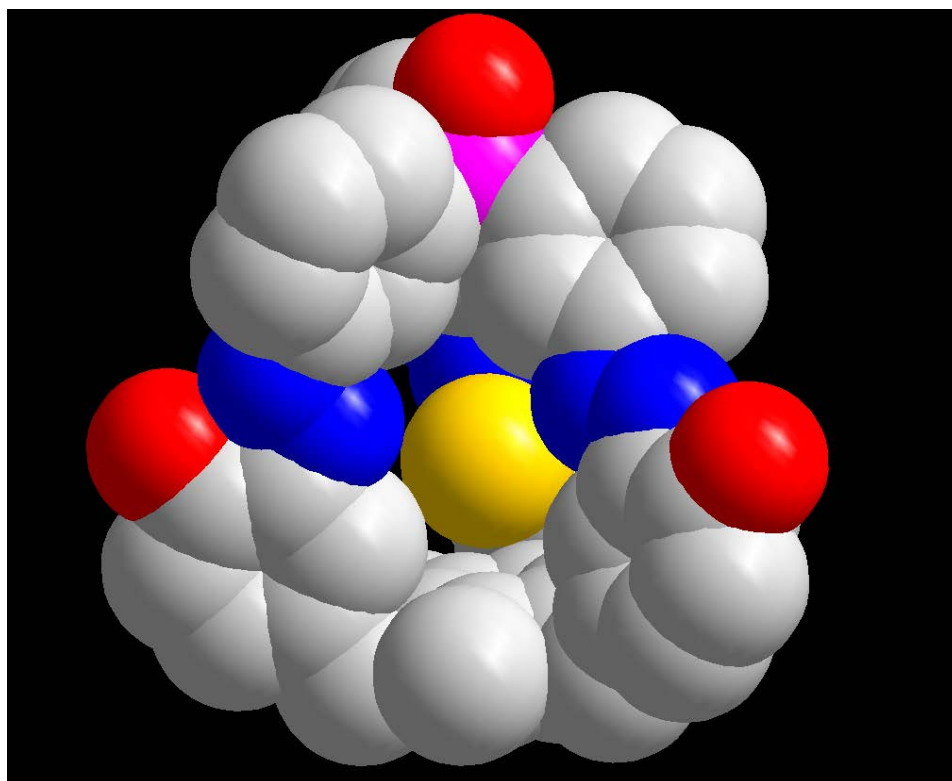


Fig. S9 The space filling model of **6**. Red, gray, blue and purple sphere represent O, C, N, and P, respectively. Yellow sphere highlights the internal cavity. Hydrogen atoms and solvent molecules are omitted for clarity.

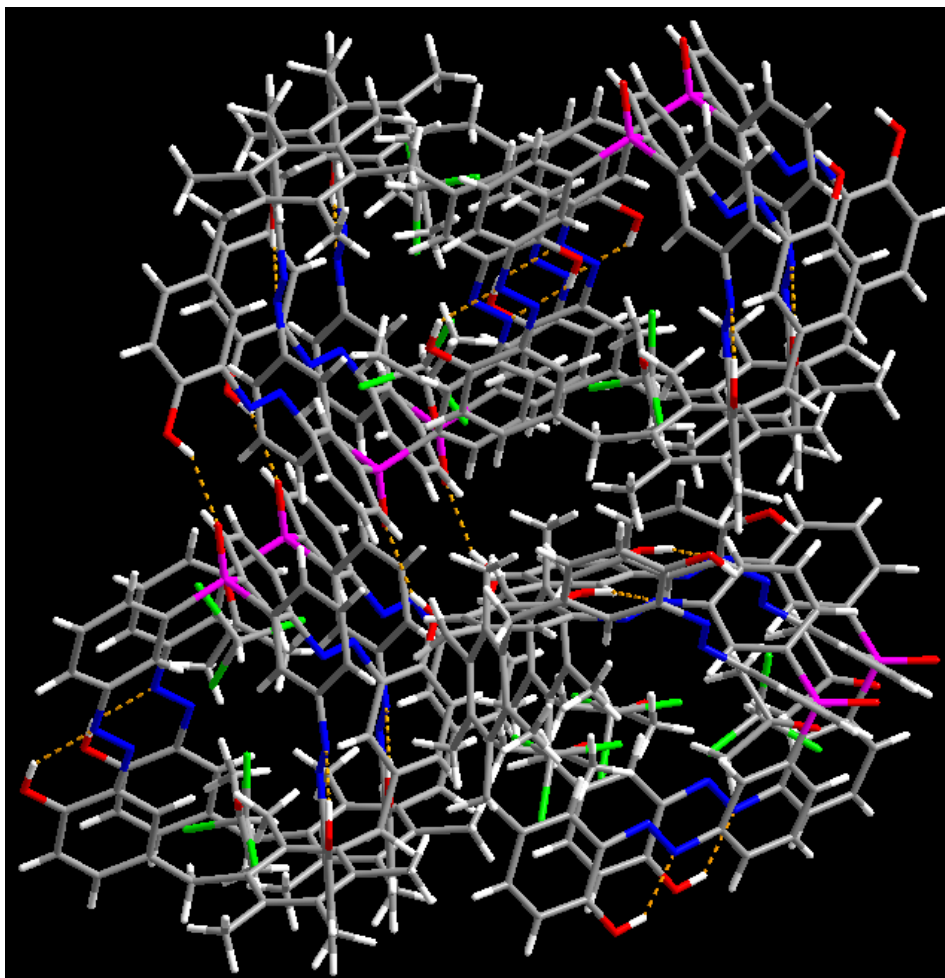


Fig. S10 A representation of the packing wires/sticks model of **6** shows only 8 cages. The two hydroxyl groups in each cage form intramolecular hydrogen bond with their own azo bonds. Another hydroxyl group forms intermolecular hydrogen bond with the P=O group. This White, Red, gray, blue and purple atoms represent H, O, C, N, and P, respectively.

7. Supporting reference

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8. Supplementary NMR and HRMS spectra

