Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2021

Supplementary Information

Pillar[6]quinone: Facile Synthesis, Crystal Structures and Electrochemical Properties

Tomoki Hirohata,[1] Naoki Shida,[1] Hidehiro Uekusa,[2] Nobuhiro Yasuda,[3] Hirotomo Nishihara,[4] Tomoki Ogoshi,[5] Ikuyoshi Tomita,[1] and Shinsuke Inagi[1,6]*

[1]Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

[2]Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8551, Japan

[3]Diffraction and Scattering Division, Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

[4]Advanced Institute for Materials Research (WPI-AIMR) / Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

[5]Department of Synthetic and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[6]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Contents

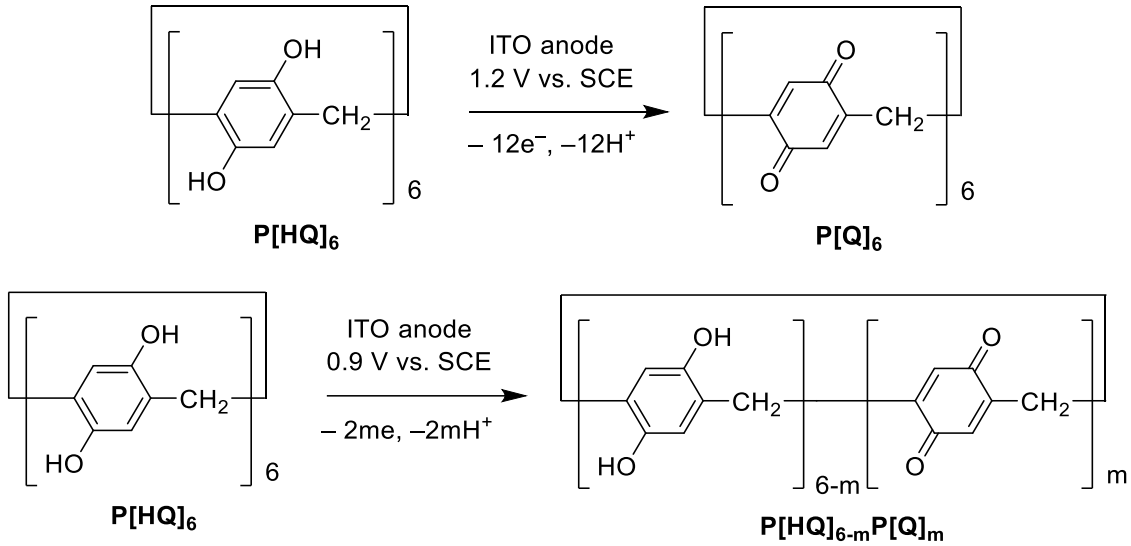
Experimental

1. General considerations

All reagents, solvents, and indium-tin-oxide (ITO) plate were obtained from commercial source and used without further purification. 1,4-Dihydroxypillar[6]arene ($P[HQ]_6$) was prepared according to the reported procedures.[1,2] ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance III HD500 (^1H: 500.13 MHz, ^{13}C: 125.72 MHz) spectrometer using trifluoroacetic acid-*d* (TFA-*d*) as a solvent. The chemical shifts for ^1H and ^{13}C NMR spectra are given in δ (ppm) relative to internal tetramethylsilane and deuterated solvent, respectively. Fourier transform infrared (FT-IR) spectra were obtained on SHIMAZU IRTracer-100. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics microTOF II spectrometer. The cyclic voltammetry, square wave voltammetry, and normal pulse voltammetry measurements were performed using ALS/DY2325 BI-POTENTIOSTAT and AUTOLAB/PGSTAT101. All voltammetry measurements were carried out in the three-electrode system equipped with a glassy carbon (GC) disk working electrode (ϕ = 1 mm), a Pt plate counter electrode (10 mm × 10 mm) and an $Ag/AgNO_3$ reference electrode. Melting point was determined on a Yanaco/MP-500P. The single crystals suitable for X-ray diffraction were obtained by the electrochemical assembly on the electrode surface. The single crystal X-ray analysis was carried out on a precision diffractometer equipped with a hybrid photon counting detector, EIGER X 1M detector (DECTRIS) in the SPring-8 BL40XU beamline.[3,4] The X-ray beam (λ = 0.81078 Å) was focused to 1.32 (vertical) × 2.95 (horizontal) μm using a zoneplate. An empirical absorption correction was carried out by the MULTI-SCAN method. The structure was solved by the SHELXT and refined by full-matrix least squares method by SHELXL. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku/SmartLab with CuKα radiation. 3D laser confocal microscope observation was performed with an Olympus/OLS4100. All theoretical calculations were performed using Gaussian 16 software. Geometry optimizations and frequency calculations were performed for all compounds at the ωB97XD level of theory using 6-311+G(d,p) basis set for all atoms. UV-vis absorption spectra were recorded on a SHIMAZU UV-1800.

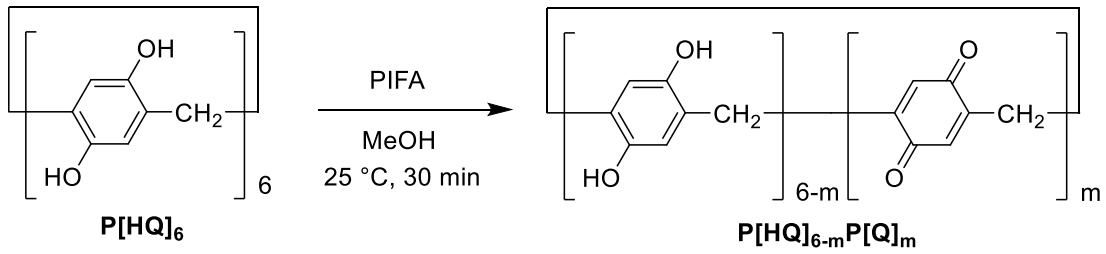
2. Synthesis

2-1. Synthesis of pillar[6]quinone ($P[Q]_6$) and partially oxidized form ($P[HQ]_{6-m}P[Q]_m$) by electrochemical oxidation[5]



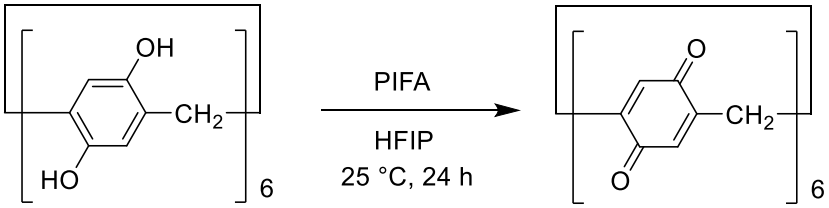
An electrolytic cell equipped with an ITO plate (10 mm × 10 mm), a Pt plate and a SCE, used as a working electrode, counter electrode, and a reference electrode, respectively, was filled with 0.1 M Bu_4NPF_6/MeOH (10 mL) and 1 mM $P[HQ]_6$. Before electrolysis, Ar bubbling was conducted for the cell. Constant potential electrolysis was carried out at 1.2 V or 0.9 V vs. SCE for 100 mC. After the electrochemical reaction, the small crystals precipitated on the electrode surface (ca. 0.1 mg) were purified by washing with acetonitrile.

2-2 Synthesis of 1,4-dihydroxypillar[6]arene-based structures by chemical oxidation[6]



To a solution of $P[HQ]_6$ (50.0 mg, 0.068 mmol) in MeOH (15 mL), phenyliodine (III) bis(trifluoroacetate) (PIFA) (88.2 mg, 0.21 mmol) was added. The mixture was stirred at 25 °C for 30 min. The resulting precipitate was isolated by filtration and washed with MeOH and $CHCl_3$ to give a brown solid of $P[HQ]_{6-m}P[Q]_m$ (27.3 mg).

2-3 Synthesis of pillar[6]quinone by chemical oxidation using 1,1,1,3,3,3-hexafluoro-2-propanol



P[HQ]$_6$ **P[Q]$_6$**

To a dispersion of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (50 mL) containing P[HQ]$_6$ (500.2 mg, 0.683 mmol) was added PIFA (2.911 g, 6.83 mmol, 10 eq.) under N_2 atmosphere and the mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under vacuum. The obtained product was dispersed into MeOH. After filtration, the residue was washed with MeOH and $CHCl_3$ to give a yellow solid of P[Q]$_6$ (394.6 mg, 80%).

P[Q]$_6$: yellow solid; ^{1}H NMR (500.13 MHz, TFA-*d*, ppm): δ = 6.86 (s, 12H, C*H*), 3.61 (s, 12H, C*H*$_2$), ^{13}C NMR (125.72 MHz, TFA-*d*, ppm): δ = 190.5 (s, *C*=O), 148.1 (s, *C*-CH$_2$), 137.8 (s, *C*H), 30.1 (s, *C*H$_2$). HRMS (ESI-TOF-MS): m/z $[M+Na]^+$ calculated for $C_{42}H_{24}O_{12}Na$: 743.1160; found: 743.1159, mp: this compound does not melt, but decomposes above 260 °C, IR (KBr, cm^{-1}): 1653, 1615, 1355, 1293, 1249, 1125, 937, 845.

2-4. Setup for the electrochemical reaction

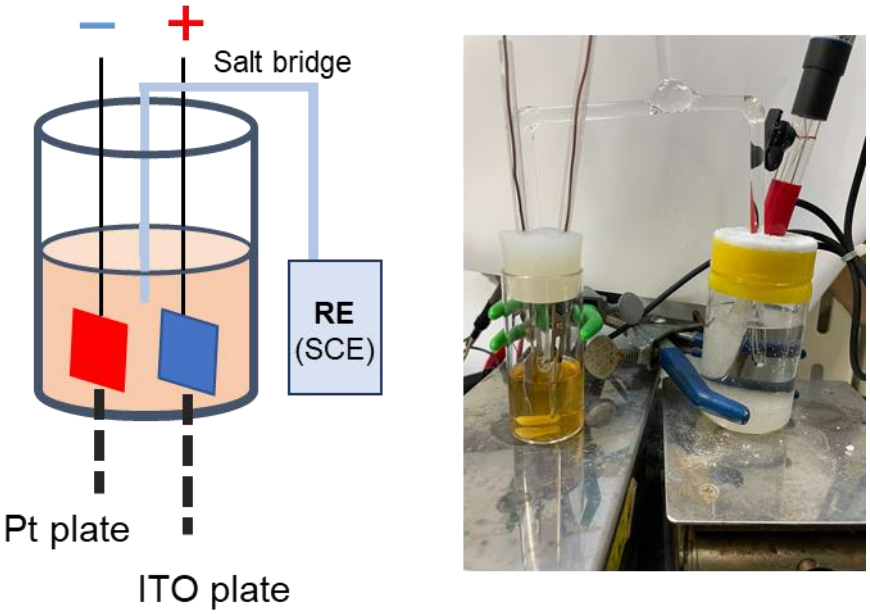


Fig. S1 The schematic illustration and photograph of electrochemical setup.

3. Laser confocal microscopy images

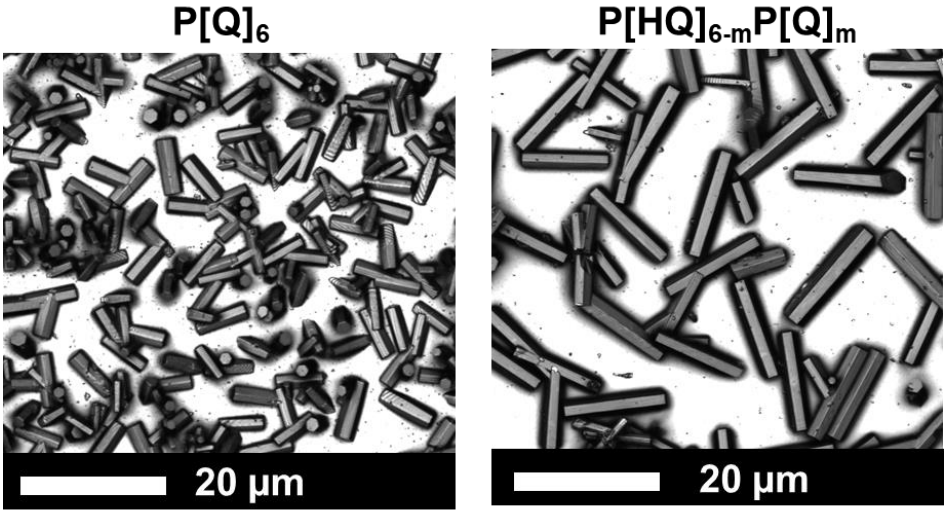


Fig. S2 3D laser confocal microscopic images of $P[Q]_6$ and $P[HQ]_{6-m}P[Q]_m$ obtained on ITO plates by electrochemical oxidation.

4. MS spectra

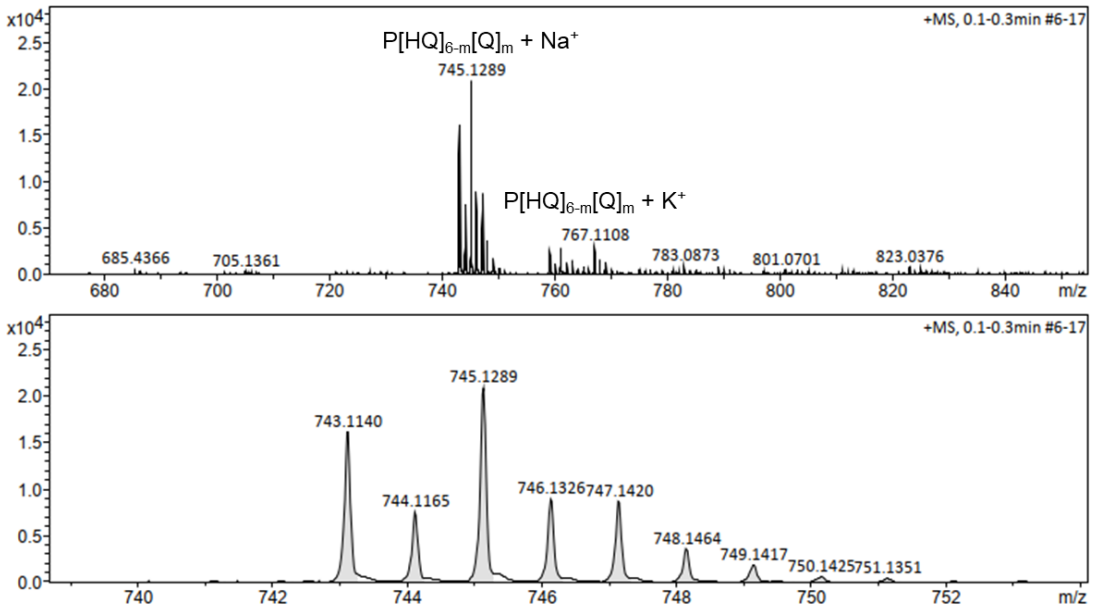


Fig. S3 ESI-MS spectra of $P[HQ]_{6-m}P[Q]_m$ synthesized by electrochemical oxidation (ion polarity is positive).

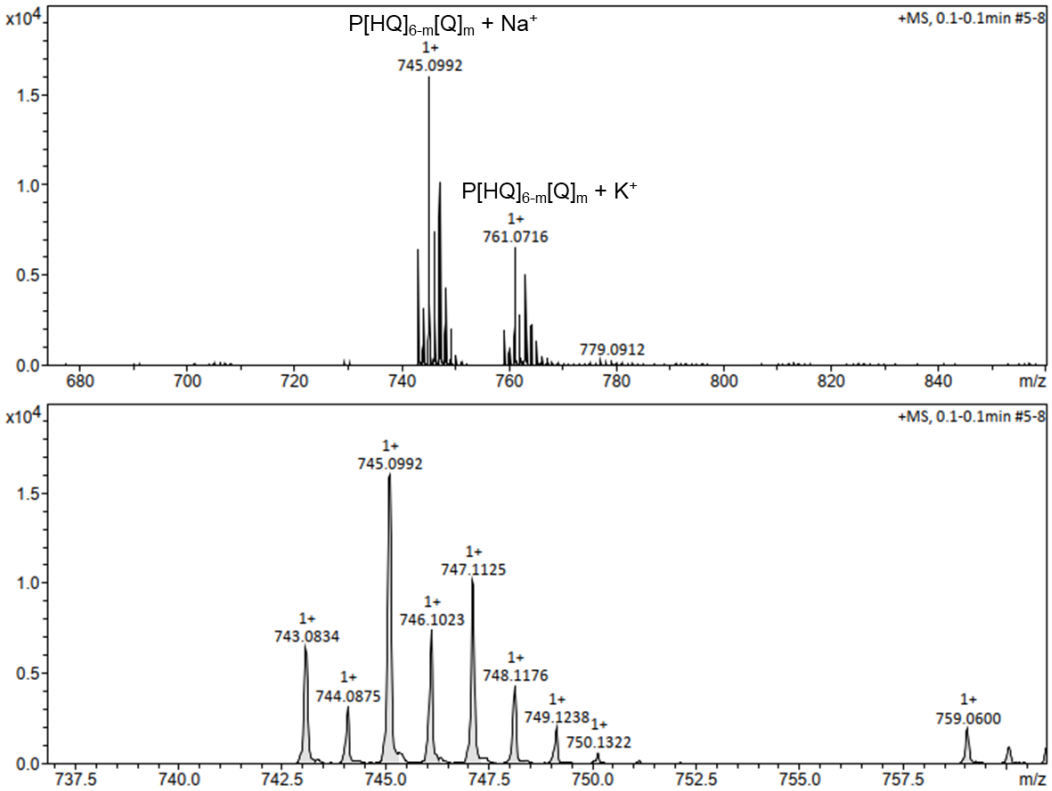


Fig. S4 ESI-MS spectra of $P[HQ]_{6-m}P[Q]_m$ synthesized by chemical oxidation (ion polarity is positive).

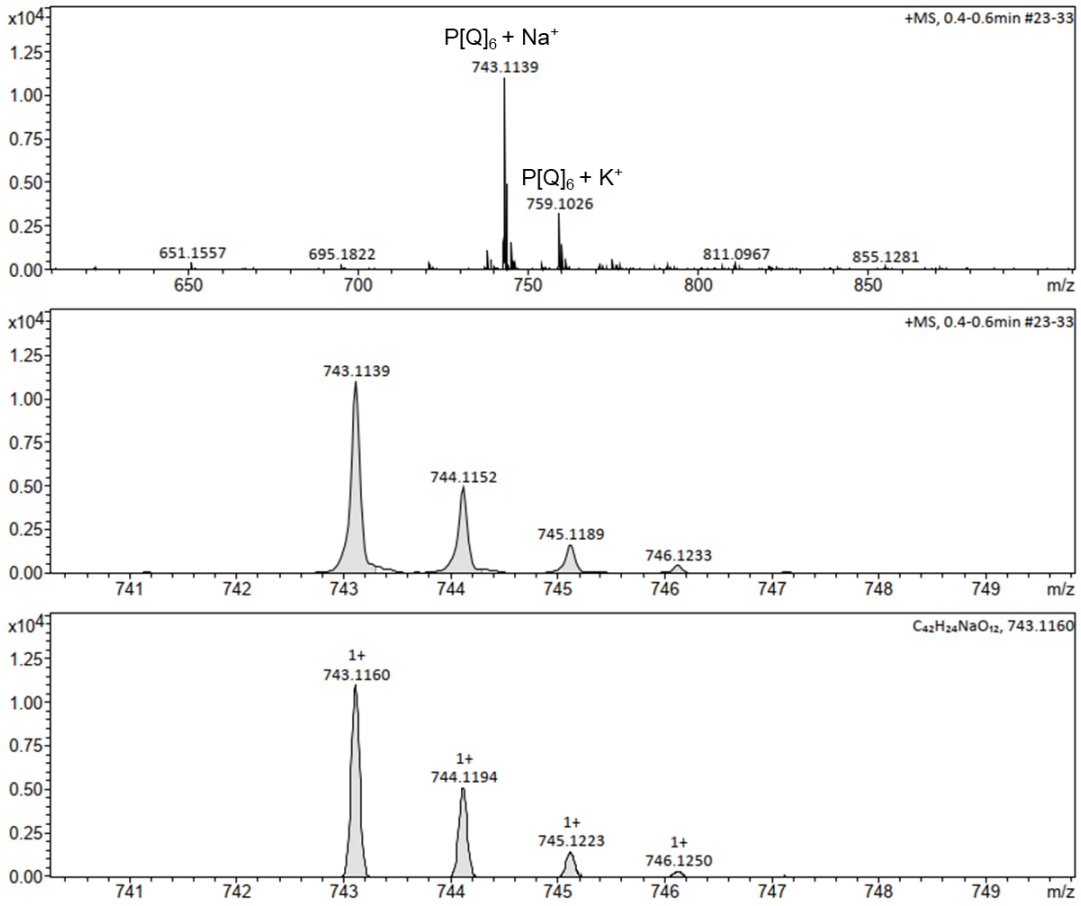


Fig. S5 ESI-MS spectra of P[Q]$_6$ synthesized by chemical oxidation (ion polarity is positive).

5. Single crystal X-ray diffraction

Table S1 Crystallographic data of $P[Q]_6$.

Crystal data	$P[Q]_6$
CCDC	2075802
Empirical Formula	C42H24O12
Formula Weight	720.61
h, k, lmax	17, 17, 5
Crystal System	Trigonal
Space Group	P-3
a, Å	14.2829(6)
b, Å	14.2829(6)
c, Å	5.2532(3)
α, deg	90
β, deg	90
γ, deg	120
Volume, Å	928.08(10)
D_{calcd}, g cm^{-3}	1.289
Z	1
F(000)	372
Data Collection	Data Collection
Temperature, K	273(2)
2 θ max, deg	58.446
Tmin/Tmax	0.3038 / 1.000
Refinement	Refinement
No. of Observed Data	1111
No. of parameters	83
R, wR2	0.0864, 0.2377
S	1.076

Although small continuous residual electron densities were observed in this channel, no molecular model could not be established for the densities in this analysis.

6. DFT calculations

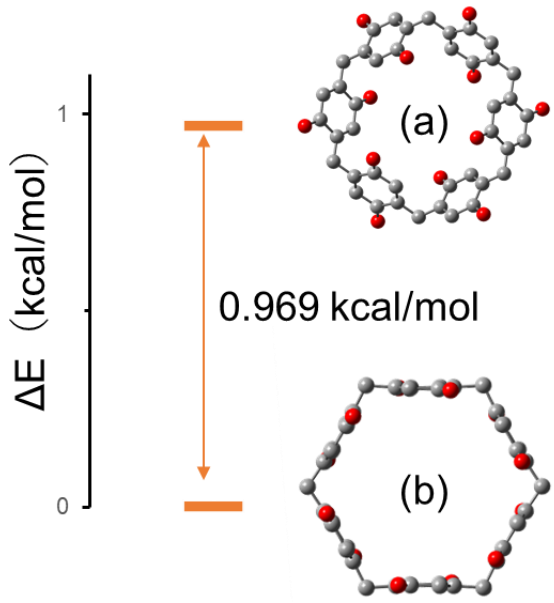


Fig. S6 The energy diagrams of P[Q]$_6$ for its (a)tilted and (b)pillar-like optimized structures obtained at the ωB97XD/6-311+G(d,p) level of theory.

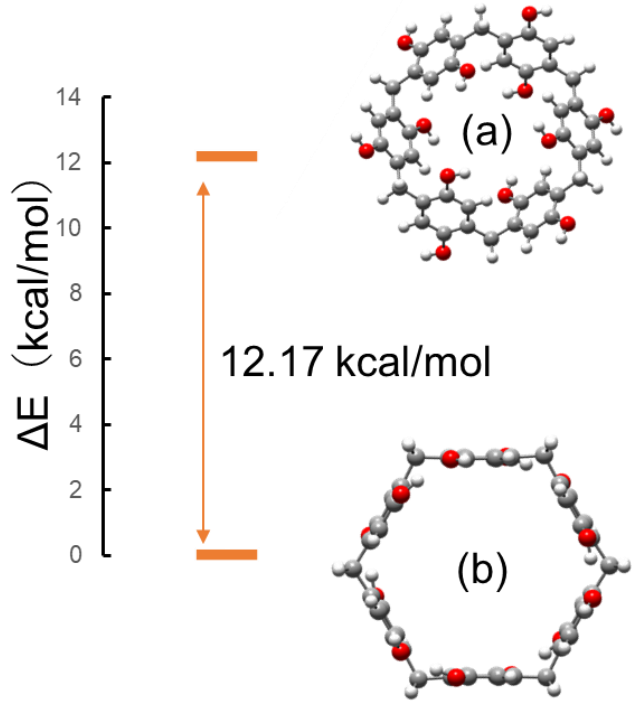


Fig. S7 The energy diagrams of P[HQ]$_6$ for its (a)tilted and (b)pillar-like optimized structures obtained at the ωB97XD/6-311+G(d,p) level of theory.

Table S2 Cartesian coordinates of the optimized structure for **P[Q]$_6$** in Fig. S6(a)

	X	Y	Z
O	-4.84737941	1.58511379	-2.28832427
O	-4.98571349	-1.0380862	2.29011016
C	-4.54924195	2.11370032	-1.23744394
C	-4.99718976	1.53187756	0.06852256
C	-5.89969571	0.32709169	0.0019123
H	-6.52919089	0.41086768	-0.88478146
C	-5.13638735	-0.9702433	-0.06634268
C	-4.75190072	-1.59746055	1.23886819
C	-4.10732578	-2.92915942	1.21233284
C	-3.82552223	-3.56051898	0.06830972
C	-3.23259433	-4.94420442	0.00075076
H	-3.53658928	-5.49950398	0.88888313
C	-1.72737735	-4.93151838	-0.067923
C	-1.03626552	-4.93729384	-1.2121003
C	-4.58951343	2.0914643	1.21192529
H	-6.53279247	0.31359053	0.88991225
C	-4.79634444	-1.57198737	-1.21047537
C	-0.48376731	5.0220669	1.21052494
C	-1.1714504	5.09259884	0.06642279
C	-2.66619908	5.27141098	-0.00185945
H	-2.99553013	5.81460496	0.8847092
C	-3.40823267	3.96154739	-0.06860475
C	-3.76146973	3.36613982	-1.21207272
O	-1.04816909	4.98583152	-2.29031946
O	-3.39105208	3.79870686	2.28810195
C	-0.44236958	4.9936009	-1.23886232
H	-2.90761266	5.85681833	-0.88985347
C	-3.75816461	3.31544673	1.23723826
O	3.79632518	3.40125324	-2.28868234
O	1.59327575	4.83924049	2.28853
C	4.10505358	2.88003141	-1.23717987
C	3.82539029	3.56041282	0.06818914
C	3.23259059	4.94414953	0.00055424
H	3.61994457	5.44737092	-0.88610767
C	1.72736657	4.93157514	-0.06799949
C	0.99184474	4.91403874	1.23717531
O	1.04798404	-4.98570051	-2.29046232
C	0.44226204	-4.99359977	-1.23896159
C	1.17144966	-5.09254328	0.06626752
C	2.666188	-5.27139923	-0.00213028
H	2.90752348	-5.85673551	-0.89019266
C	3.40825996	-3.9615543	-0.06878698
C	3.75817204	-3.31554893	1.23710591
O	-3.79597552	-3.40122862	-2.28854888
O	-1.59308256	-4.8389277	2.28858695
C	-4.10538975	-2.88030291	-1.23710105
H	-3.61997099	-5.44753116	-0.88584142
C	-0.99174734	-4.91391744	1.23719111
C	0.48386308	-5.02194608	1.2104236
H	2.9955561	-5.81468423	0.88436943
C	3.7614582	-3.36603388	-1.21220841
C	4.10714404	2.92909272	1.21224665
H	3.53669729	5.49949403	0.88862032
C	1.03616078	4.93730558	-1.21212011
O	4.84669131	-1.58447974	-2.28828125
O	4.98595324	1.03828513	2.29013888
C	4.54930358	-2.11363892	-1.23747665
C	4.99727432	-1.53193906	0.06853528
C	5.89970306	-0.32709471	0.00201752
H	6.52928391	-0.41082139	-0.88462009
C	5.13627665	0.97016305	-0.06632153
C	4.75141151	1.59724708	1.23884013
C	4.58964348	-2.09164782	1.2118936
H	6.53271028	-0.31354201	0.89008028
C	4.79629063	1.57186677	-1.2104913
H	1.52980072	4.91613434	-2.17817586
H	-0.97655461	5.05614596	2.17663813
H	5.02551548	1.1337533	-2.17638985
H	3.88885332	3.37264748	2.1781628
H	3.49874067	-3.7830508	-2.17886702
H	-1.52998485	-4.91620501	-2.17811761

H	0.97673471	-5.05596947	2.17649631
H	-5.02537086	-1.1338234	-2.17639717
H	-3.88893248	-3.37261951	2.17826925
H	-3.49880931	3.78327284	-2.17869674
H	-4.86315362	1.68082498	2.17833283
H	4.86332574	-1.68111341	2.17833389
O	3.39190009	-3.79945568	2.28796535

Table S3 Cartesian coordinates of the optimized structure for **P[Q]$_6$** in Fig. S6(b)

	X	Y	Z
O	-4.84737941	1.58511379	-2.28832427
O	-4.98571349	-1.0380862	2.29011016
C	-4.54924195	2.11370032	-1.23744394
C	-4.99718976	1.53187756	0.06852256
C	-5.89969571	0.32709169	0.0019123
H	-6.52919089	0.41086768	-0.88478146
C	-5.13638735	-0.9702433	-0.06634268
C	-4.75190072	-1.59746055	1.23886819
C	-4.10732578	-2.92915942	1.21233284
C	-3.82552223	-3.56051898	0.06830972
C	-3.23259433	-4.94420442	0.00075076
H	-3.53658928	-5.49950398	0.88888313
C	-1.72737735	-4.93151838	-0.067923
C	-1.03626552	-4.93729384	-1.2121003
C	-4.58951343	2.0914643	1.21192529
H	-6.53279247	0.31359053	0.88991225
C	-4.79634444	-1.57198737	-1.21047537
C	-0.48376731	5.0220669	1.21052494
C	-1.1714504	5.09259884	0.06642279
C	-2.66619908	5.27141098	-0.00185945
H	-2.99553013	5.81460496	0.8847092
C	-3.40823267	3.96154739	-0.06860475
C	-3.76146973	3.36613982	-1.21207272
O	-1.04816909	4.98583152	-2.29031946
O	-3.39105208	3.79870686	2.28810195
C	-0.44236958	4.9936009	-1.23886232
H	-2.90761266	5.85681833	-0.88985347
C	-3.75816461	3.31544673	1.23723826
O	3.79632518	3.40125324	-2.28868234
O	1.59327575	4.83924049	2.28853
C	4.10505358	2.88003141	-1.23717987
C	3.82539029	3.56041282	0.06818914
C	3.23259059	4.94414953	0.00055424
H	3.61994457	5.44737092	-0.88610767
C	1.72736657	4.93157514	-0.06799949
C	0.99184474	4.91403874	1.23717531
O	1.04798404	-4.98570051	-2.29046232
C	0.44226204	-4.99359977	-1.23896159
C	1.17144966	-5.09254328	0.06626752
C	2.666188	-5.27139923	-0.00213028
H	2.90752348	-5.85673551	-0.89019266
C	3.40825996	-3.9615543	-0.06878698
C	3.75817204	-3.31554893	1.23710591
O	-3.79597552	-3.40122862	-2.28854888
O	-1.59308256	-4.8389277	2.28858695
C	-4.10538975	-2.88030291	-1.23710105
H	-3.61997099	-5.44753116	-0.88584142
C	-0.99174734	-4.91391744	1.23719111
C	0.48386308	-5.02194608	1.2104236
H	2.9955561	-5.81468423	0.88436943
C	3.7614582	-3.36603388	-1.21220841
C	4.10714404	2.92909272	1.21224665
H	3.53669729	5.49949403	0.88862032
C	1.03616078	4.93730558	-1.21212011
O	4.84669131	-1.58447974	-2.28828125
O	4.98595324	1.03828513	2.29013888
C	4.54930358	-2.11363892	-1.23747665
C	4.99727432	-1.53193906	0.06853528
C	5.89970306	-0.32709471	0.00201752
H	6.52928391	-0.41082139	-0.88462009
C	5.13627665	0.97016305	-0.06632153
C	4.75141151	1.59724708	1.23884013
C	4.58964348	-2.09164782	1.2118936
H	6.53271028	-0.31354201	0.89008028
C	4.79629063	1.57186677	-1.2104913
H	1.52980072	4.91613434	-2.17817586
H	-0.97655461	5.05614596	2.17663813
H	5.02551548	1.1337533	-2.17638985
H	3.88885332	3.37264748	2.1781628
H	3.49874067	-3.7830508	-2.17886702
H	-1.52998485	-4.91620501	-2.17811761

H	0.97673471	-5.05596947	2.17649631
H	-5.02537086	-1.1338234	-2.17639717
H	-3.88893248	-3.37261951	2.17826925
H	-3.49880931	3.78327284	-2.17869674
H	-4.86315362	1.68082498	2.17833283
H	4.86332574	-1.68111341	2.17833389
O	3.39190009	-3.79945568	2.28796535

Table S4 Cartesian coordinates of the optimized structure for **P[HQ]$_6$** in Fig. S7(a)

	X	Y	Z
C	4.50470277	2.1638445	-0.41164319
C	5.51887758	1.3852332	-0.96943521
C	5.75386393	0.0968149	-0.50582516
H	6.52978224	-0.5078897	-0.9699556
C	5.00590057	-0.4561491	0.53056669
C	4.01642791	0.33606218	1.10889244
C	3.77375204	1.61975208	0.637736
H	2.97555916	2.20818009	1.08206051
C	4.22703927	3.54974154	-0.96259184
H	5.03051756	4.2264215	-0.65328684
H	4.27536096	3.49834069	-2.05291257
C	0.37779012	4.98047475	0.41213925
C	1.55913897	5.47168053	0.96804971
C	2.79249008	5.03109906	0.50451074
H	3.70414567	5.40265539	0.96706275
C	2.89750336	4.1047649	-0.52996757
C	1.71667656	3.64160279	-1.1063813
C	0.48358031	4.07320673	-0.63529569
H	-0.4251965	3.67456488	-1.07805621
C	-0.96112479	5.43317013	0.96316305
H	-1.14494127	6.46755687	0.65430834
H	-0.89245112	5.44887717	2.05350192
C	4.12667975	-2.81761602	0.41220791
C	3.95985728	-4.08594866	0.96847056
C	2.96088907	-4.9328039	0.50474994
H	2.82561997	-5.90782318	0.96753414
C	2.10697544	-4.56001177	-0.53024048
C	2.2976996	-3.30613021	-1.10687035
C	3.2887282	-2.45497743	-0.63557245
H	3.39896655	-1.46883422	-1.07850097
C	5.18917885	-1.88527813	0.96283528
H	6.1764262	-2.24354465	0.65279552
H	5.16946287	-1.95308873	2.05314403
C	-0.37778965	-4.98047447	-0.41213985
C	-1.55913874	-5.47168037	-0.96804974
C	-2.79248968	-5.03109869	-0.50451051
H	-3.70414543	-5.40265523	-0.96706202
C	-2.89750259	-4.10476428	0.5299676
C	-1.71667553	-3.64160189	1.10638062
C	-0.48357945	-4.07320583	0.63529458
H	0.42519749	-3.67456352	1.07805441
C	0.96112502	-5.43317024	-0.96316389
H	1.14494122	-6.46755708	-0.65430922
H	0.89245119	-5.44887728	-2.05350274
C	-4.12667985	2.81761562	-0.41220775
C	-3.95985705	4.08594793	-0.96847106
C	-2.96088861	4.93280318	-0.50475097
H	-2.8256195	5.90782228	-0.96753553
C	-2.10697502	4.56001139	0.53023961
C	-2.29769947	3.30613019	1.10687013
C	-3.28872823	2.45497735	0.63557267
H	-3.39896675	1.46883442	1.07850178
C	-5.18917956	1.885278	-0.96283453
H	-6.17642657	2.24354497	-0.65279422
H	-5.16946424	1.95308864	-2.05314331
C	-4.50470303	-2.1638445	0.41164382
C	-5.51887489	-1.38523173	0.96943917
C	-5.7538616	-0.09681352	0.50582907
H	-6.52977721	0.5078924	0.96996226
C	-5.00590161	0.4561489	-0.53056606
C	-4.01643241	-0.33606406	-1.10889541
C	-3.77375611	-1.61975385	-0.63773895
H	-2.97556575	-2.20818316	-1.08206625
C	-4.22703833	-3.54974118	0.96259278
H	-5.03051662	-4.22642167	0.65328893
H	-4.27535885	-3.49833988	2.05291355
O	1.44260466	6.38345108	1.98281718
H	2.31280772	6.60820753	2.31408463
O	1.82050612	2.72901981	-2.12147495
H	0.9426897	2.51302904	-2.43917014
O	-4.80699846	4.44155334	-1.98360414

H	-4.56552212	5.30719975	-2.31503972
O	-1.45621902	2.93914654	2.12235272
H	-1.70892973	2.07119129	2.44004633
O	-6.2485185	-1.94085932	1.98607075
H	-6.87691156	-1.29884796	2.31841613
O	-3.27973443	0.20901954	-2.12582673
H	-2.65475977	-0.44375063	-2.44432387
O	-1.82050465	-2.72901821	2.12147373
H	-0.9426884	-2.51303178	2.43917234
O	-1.44260481	-6.38345129	-1.9828169
H	-2.31280792	-6.608207	-2.31408475
O	4.80699853	-4.44155436	1.98360367
H	4.56552402	-5.30720219	2.31503692
O	1.45621912	-2.93914634	-2.12235281
H	1.70892666	-2.07118892	-2.440043
O	3.27972618	-0.20902316	2.12582012
H	2.6547509	0.44374673	2.44431661
O	6.24852485	1.94086249	-1.98606328
H	6.87691971	1.29885201	-2.31840693

Table S5 Cartesian coordinates of the optimized structure for **P[HQ]$_6$** in Fig. S7(b)

	X	Y	Z
O	3.10695738	3.97008316	2.48253163
H	3.78587281	3.27945393	2.46167329
C	2.61970184	4.22266587	1.24093388
C	3.33406504	3.97131554	0.06454976
C	4.7463146	3.42198948	0.07245944
H	5.28494107	3.8036681	0.94357165
C	4.84005128	1.91122494	0.0368068
C	4.85150756	1.22772408	-1.17106127
O	4.98971628	-0.70646954	-2.4821179
H	4.73228476	-1.64007348	-2.46090402
C	4.96519969	-0.15801092	-1.2406183
C	5.10518572	-0.90216871	-0.0642336
C	5.33622624	-2.39974893	-0.07254368
H	5.93615893	-2.67460081	-0.9438476
C	4.07517063	-3.23697679	-0.03699767
C	3.48911135	-3.58875969	1.17089926
O	4.90792329	1.83762095	2.40691497
H	4.91921709	1.21630556	3.13649028
C	2.72345933	4.28059743	-1.14977345
H	5.26797502	3.81400262	-0.8037855
C	4.92994937	1.15729901	1.20407224
O	-1.88371789	4.67598859	-2.48219467
H	-0.94641582	4.91965031	-2.46120156
C	-2.34619105	4.38050952	-1.24060134
C	-1.77179556	4.87409865	-0.06425233
C	-0.59017106	5.82273661	-0.07262201
H	-0.65134238	6.47922951	-0.94436512
C	0.76512424	5.14869163	-0.03662371
C	1.36279723	4.81712587	1.17127414
O	0.86292869	5.17068722	-2.40665318
H	1.40638793	4.86937644	-3.13624835
C	-2.34502992	4.50004001	1.15007481
H	-0.66892466	6.47118089	0.80311577
C	1.46305241	4.84940683	-1.20383959
O	-4.98971628	0.70646954	2.4821179
H	-4.73228476	1.64007348	2.46090402
C	-4.96519969	0.15801092	1.2406183
C	-5.10518572	0.90216871	0.0642336
C	-5.33622624	2.39974893	0.07254368
H	-5.93615893	2.67460081	0.9438476
C	-4.07517063	3.23697679	0.03699767
C	-3.48911135	3.58875969	-1.17089926
O	1.88371789	-4.67598859	2.48219467
H	0.94641582	-4.91965031	2.46120156
C	2.34619105	-4.38050952	1.24060134
C	1.77179556	-4.87409865	0.06425233
C	0.59017106	-5.82273661	0.07262201
H	0.65134238	-6.47922951	0.94436512
C	-0.76512424	-5.14869163	0.03662371
C	-1.36279723	-4.81712587	-1.17127414
O	4.04547921	-3.33304958	-2.40711591
H	3.51284902	-3.65327527	-3.13664132
C	5.06782963	-0.21865288	1.15004317
H	5.93682368	-2.65556888	0.8034905
C	3.46741942	-3.69227103	-1.20422873
O	-0.86292869	-5.17068722	2.40665318
H	-1.40638793	-4.86937644	3.13624835
C	2.34502992	-4.50004001	-1.15007481
H	0.66892466	-6.47118089	-0.80311577
C	-1.46305241	-4.84940683	1.20383959
O	-4.04547921	3.33304958	2.40711591
H	-3.51284902	3.65327527	3.13664132
C	-5.06782963	0.21865288	-1.15004317
H	-5.93682368	2.65556888	-0.8034905
C	-3.46741942	3.69227103	1.20422873
O	-4.90792329	-1.83762095	-2.40691497
H	-4.91921709	-1.21630556	-3.13649028
C	-2.72345933	-4.28059743	1.14977345
C	-3.33406504	-3.97131554	-0.06454976
C	-4.7463146	-3.42198948	-0.07245944
H	-5.26797502	-3.81400262	0.8037855

C	-4.84005128	-1.91122494	-0.0368068
C	-4.92994937	-1.15729901	-1.20407224
O	-3.10695738	-3.97008316	-2.48253163
H	-3.78587281	-3.27945393	-2.46167329
C	-2.61970184	-4.22266587	-1.24093388
H	-5.28494107	-3.8036681	-0.94357165
C	-4.85150756	-1.22772408	1.17106127
H	0.85316346	5.02975178	2.10498895
H	3.26566182	4.08983117	-2.07291419
H	-3.92775487	3.25322401	-2.10458655
H	-1.9090745	4.87472802	2.07318329
H	-5.1740797	0.7835049	-2.07318697
H	-4.78056353	-1.77538566	2.10475248
H	-3.26566182	-4.08983117	2.07291419
H	-0.85316346	-5.02975178	-2.10498895
H	1.9090745	-4.87472802	-2.07318329
H	3.92775487	-3.25322401	2.10458655
H	5.1740797	-0.7835049	2.07318697
H	4.78056353	1.77538566	-2.10475248

7. UV-vis spectra

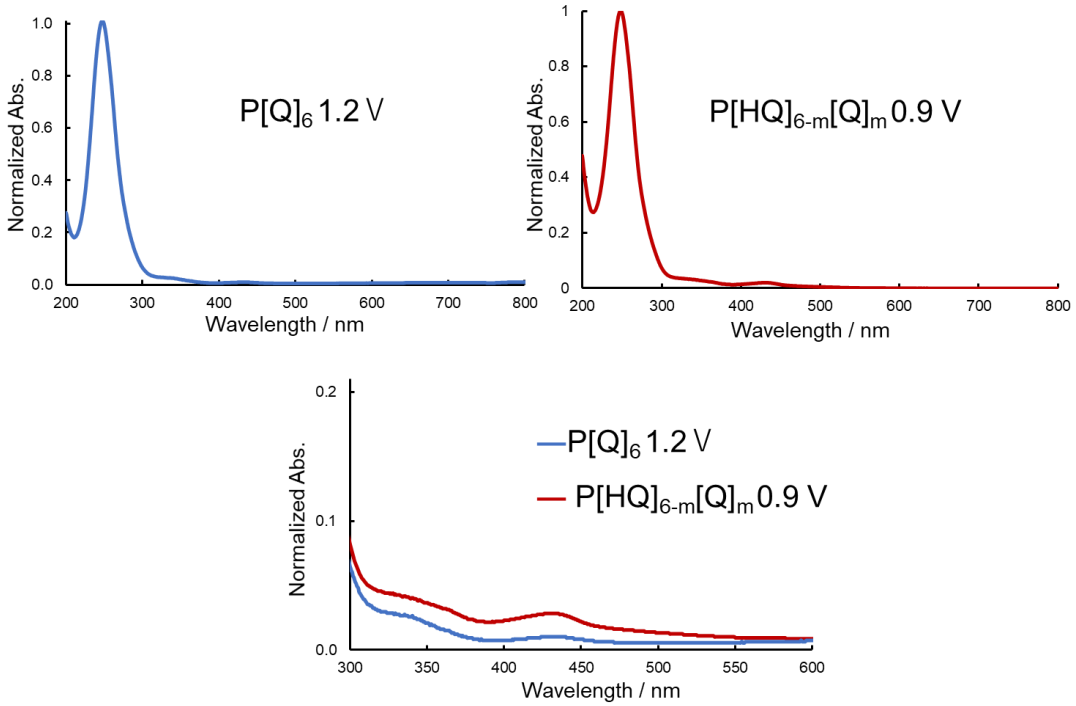


Fig. S8 UV-vis absorption spectra of $P[Q]_6$ and $P[HQ]_{6-m}P[Q]_m$ synthesized by electrochemical oxidation, measured in HFIP.

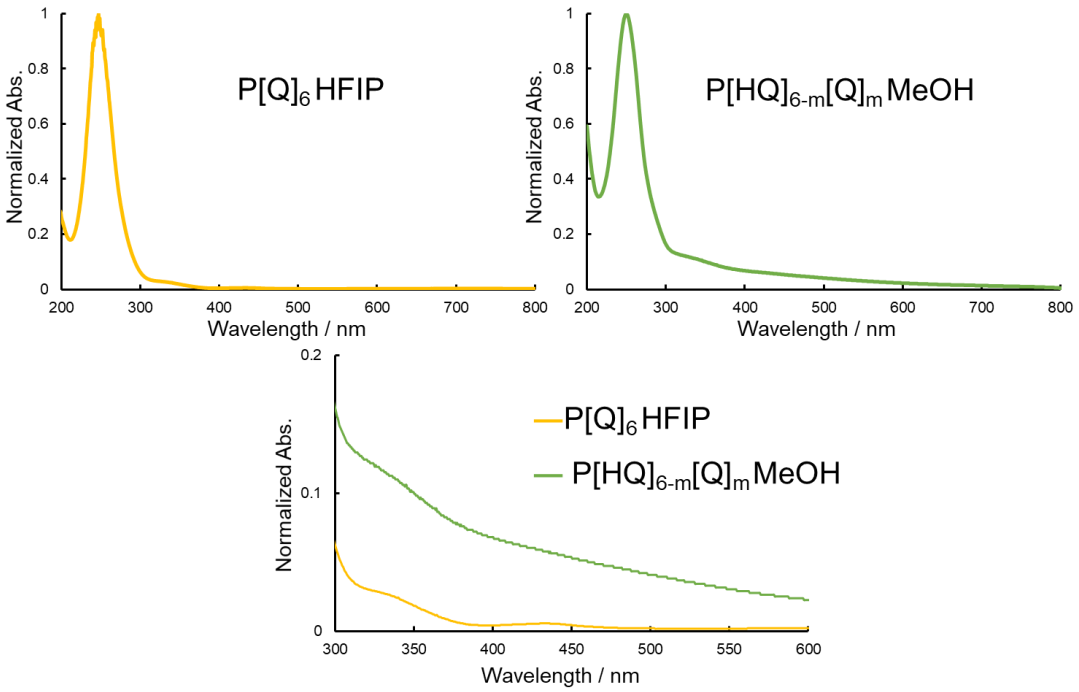


Fig. S9 UV-vis absorption spectra of $P[Q]_6$ and $P[HQ]_{6-m}P[Q]_m$ synthesized by chemical oxidation, measured in HFIP.

8. Powder X-ray diffractions

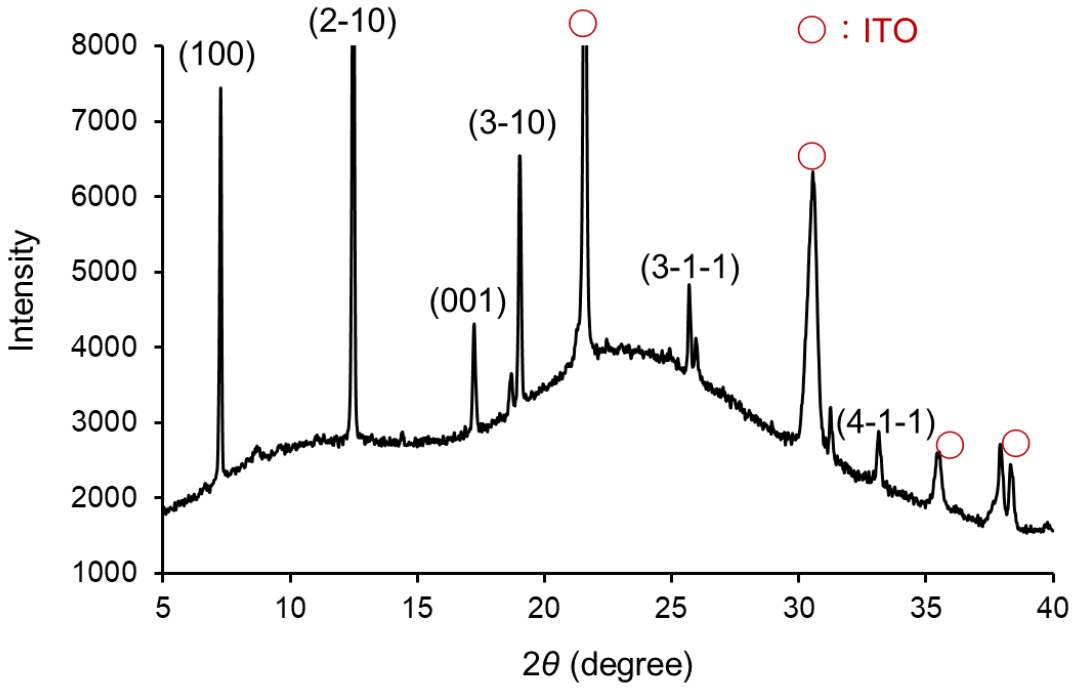


Fig. S10 Powder X-ray diffraction pattern of $P[Q]_6$ on an ITO plate obtained by electrochemical oxidation.

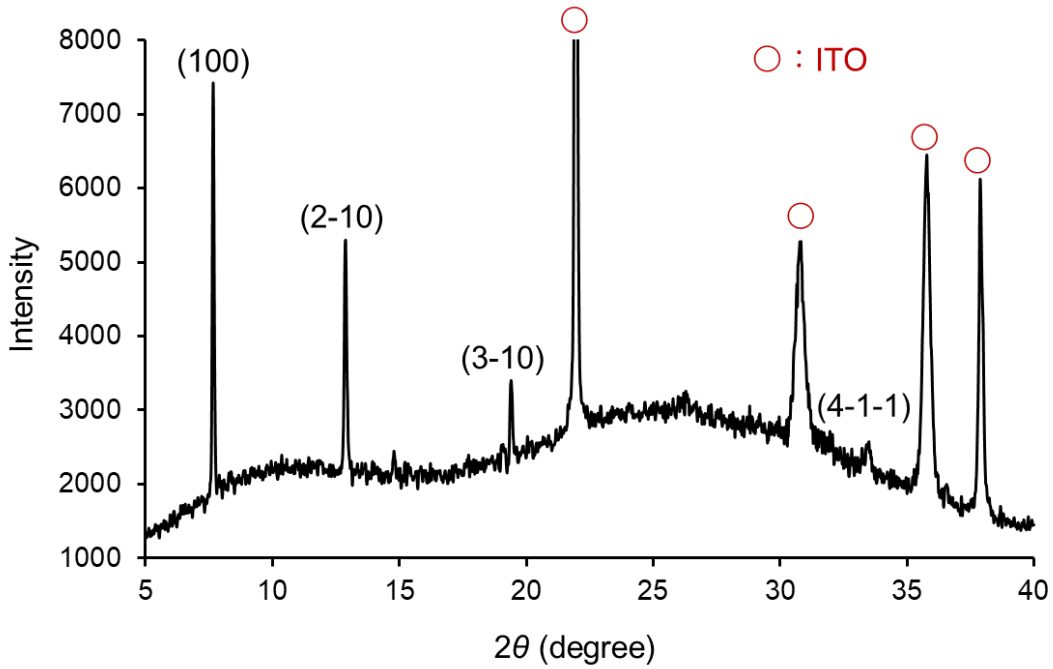


Fig. S11 Powder X-ray diffraction pattern of $P[HQ]_{6-m}P[Q]_m$ on an ITO plate obtained by electrochemical oxidation.

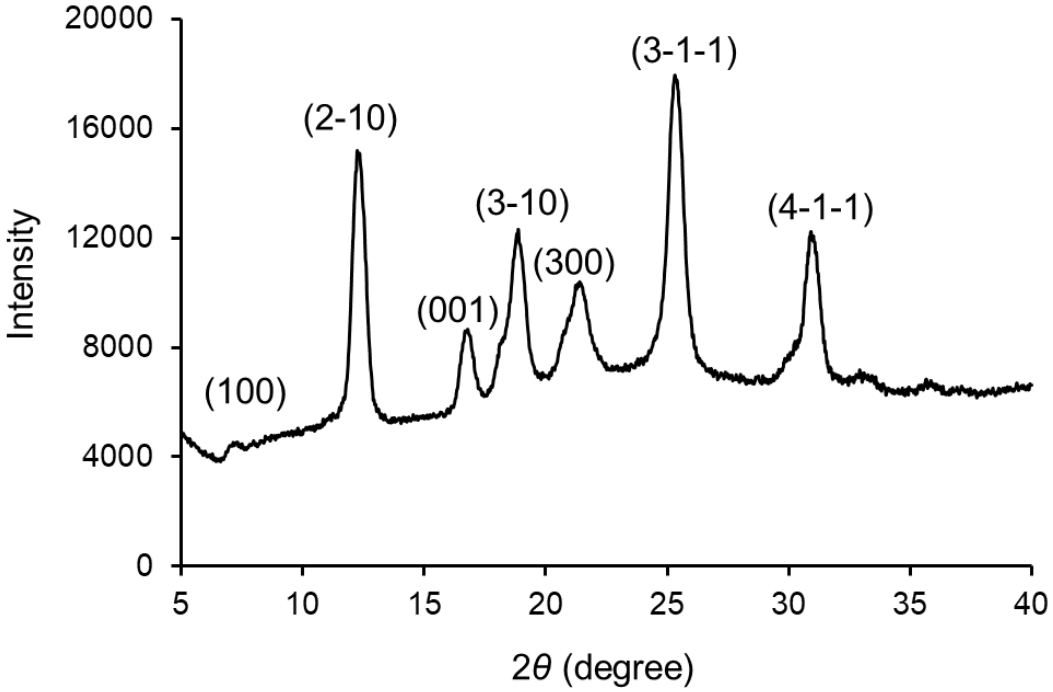


Fig. S12 Powder X-ray diffraction pattern of $P[Q]_6$ obtained by chemical oxidation.

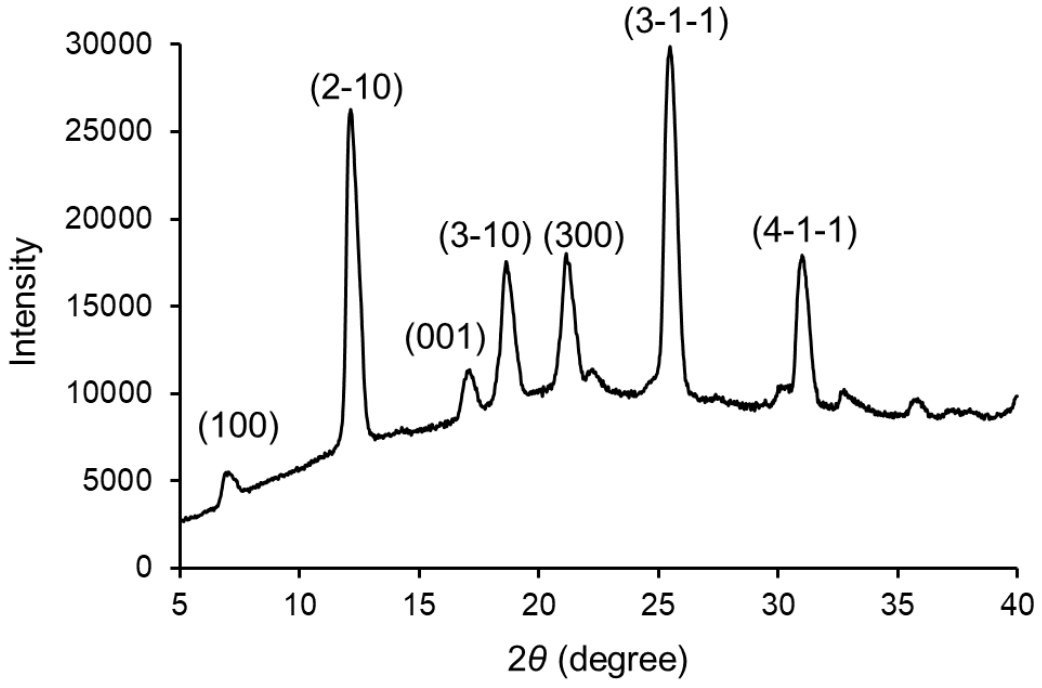


Fig. S13 Powder X-ray diffraction pattern of $P[HQ]_{6-m}P[Q]_m$ by chemical oxidation.

9. Electrochemical properties of *p*-xyloquinone

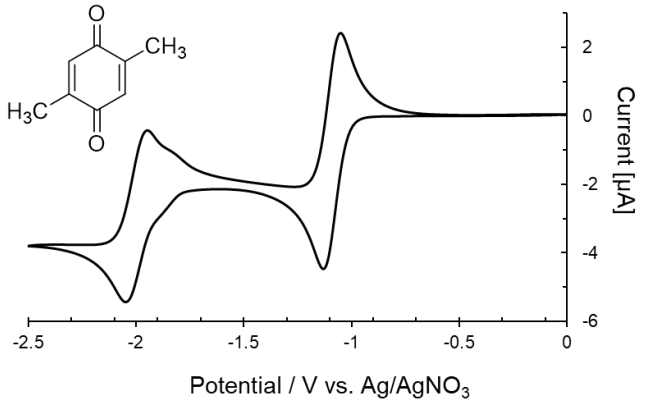


Fig. S14 Cyclic voltammogram of *p*-xyloquinone (1 mM) measured in 0.1 M Bu_4NPF_6/DMF using an GC disk (φ = 1 mm) as a working electrode at a scan rate of 20 mV/s.

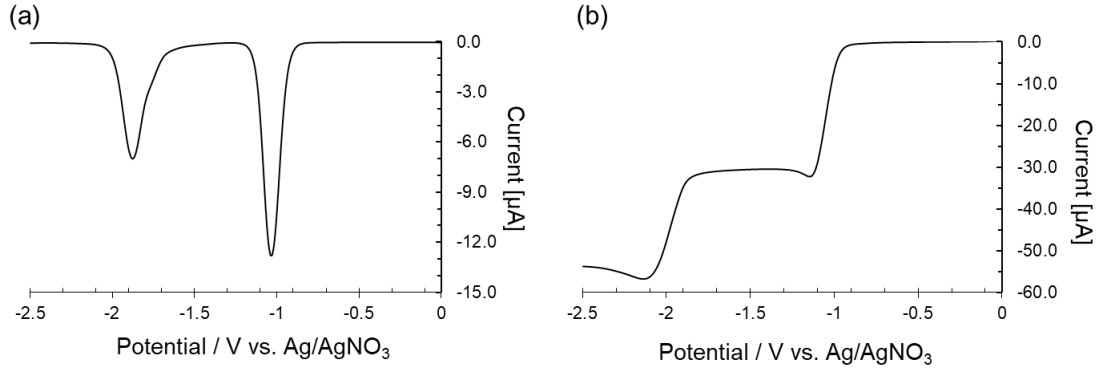


Fig. S15 Cathodic voltammetric behavior of *p*-xyloquinone (1 mM) measured in 0.1 M Bu_4NPF_6/DMF using an GC disk (φ = 1 mm) as a working electrode at a scan rate of 20 mV/s. (a) Square wave voltammetry. (b) Normal pulse voltammetry.

10. NMR charts

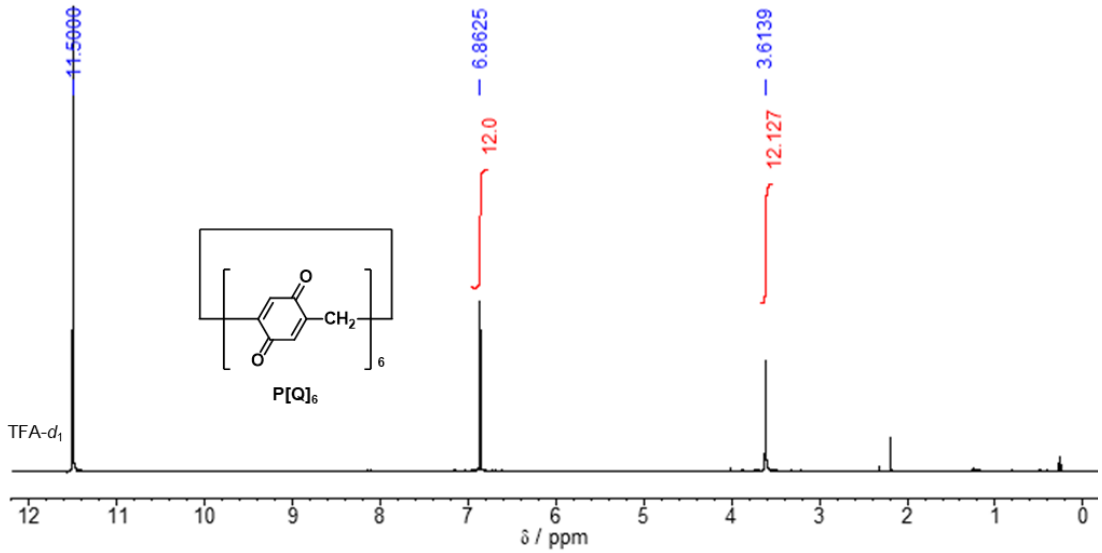


Fig. S16 ^{1}H NMR spectrum (500.13 MHz, TFA-*d*) of P[Q]$_6$ synthesized by chemical oxidation.

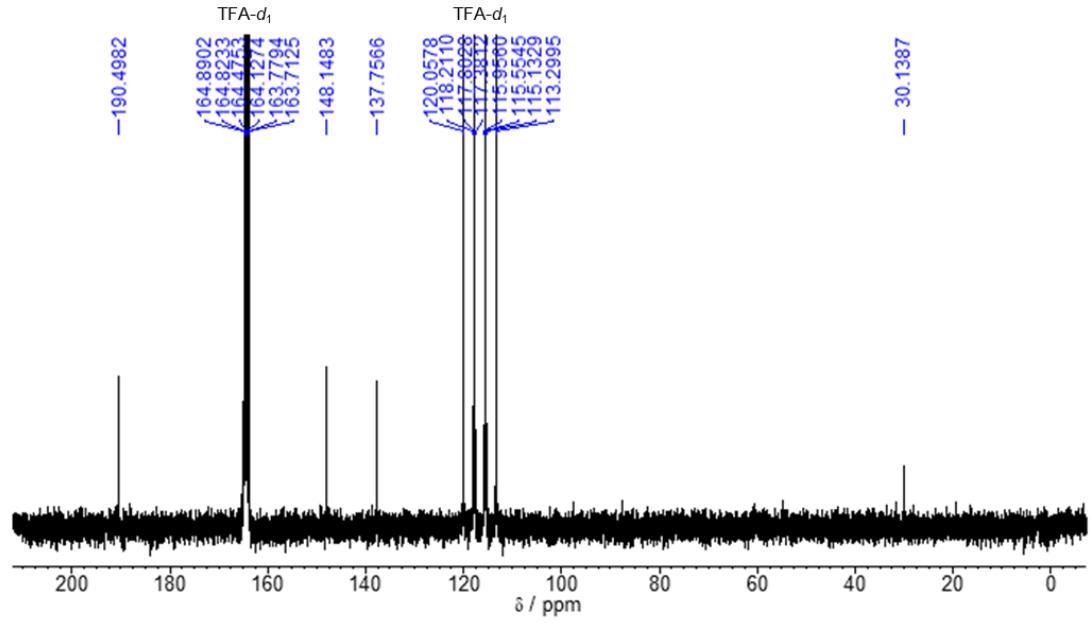


Fig. S17 ^{13}C NMR spectrum (125.76 MHz, TFA-*d*) of P[Q]$_6$ synthesized by chemical oxidation.

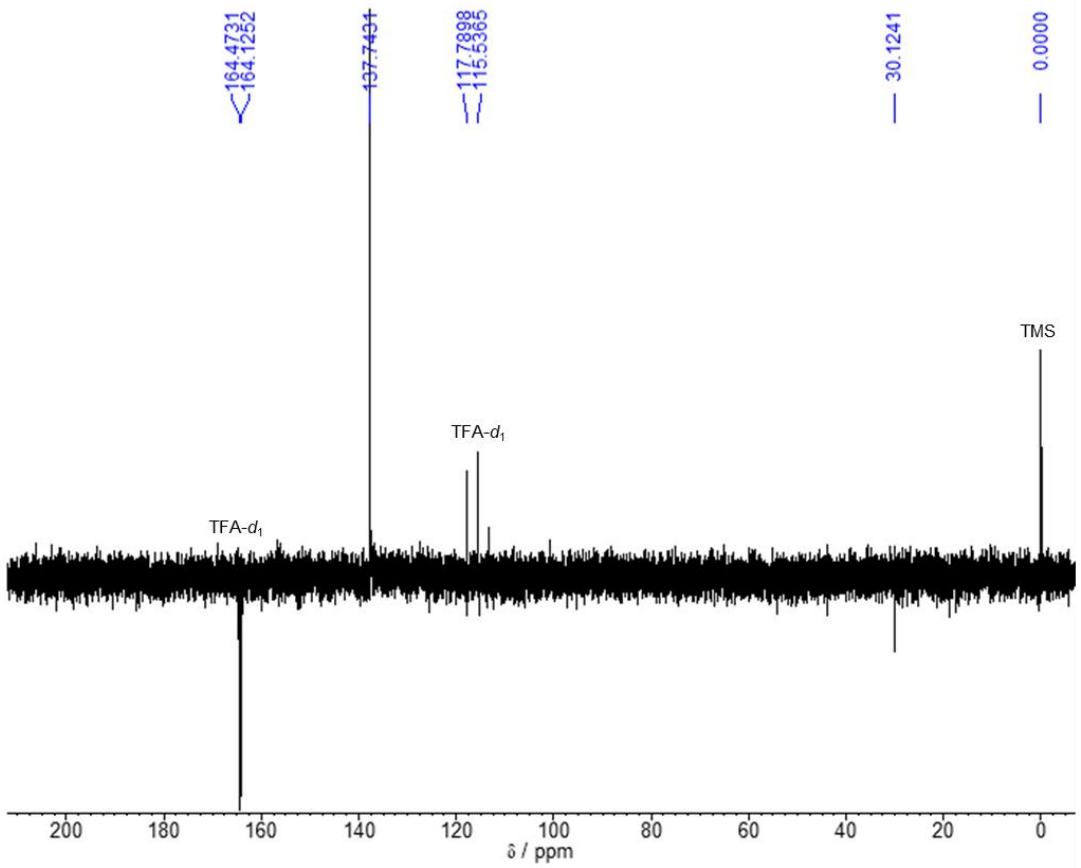


Fig. S18 DEPT-135 NMR spectrum (125.76 MHz, TFA-*d*) of P[Q]$_6$ synthesized by chemical oxidation.

Supplementary References

[1] J. Cao, Y. Shang, B. Qi, X. Sun, L. Zhang, H. Liu, H. Zhang and X. Zhou, *RSC Adv.*, 2015, **5**, 9993-9996.

[2] Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J. Hou, *Org. Lett.*, 2012, **14**, 1532–1535.

[3] N. Yasuda, H. Murayama, Y. Fukuyama, J. E. Kim, S. Kimura, K. Toriumi, Y. Tanaka, Y. Moritomo, Y. Kuroiwa, K. Kato, H. Tanaka and M, Takata, *J. Synchrotron Rad.*, 2009, **16**, 352–357.

[4] N. Yasuda, Y. Fukuyama, K. Toriumi, S. Kimura and M. Takata, *AIP Conference Proceedings*, 2010, **1234**, 147–150.

[5] C. Tsuneishi, Y. Koizumi, R. Sueto, H. Nishiyama, K. Yasuhara, T. Yamagishi, T. Ogoshi, I. Tomita and S. Inagi, *Chem. Commun.,* 2017, **53**, 7454–7456.

[6] T. Ogoshi, K. Yoshikoshi, R. Sueto, H. Nishihara and T. Yamagishi, *Angew. Chem. Int. Ed.,* 2015, **54**, 6466–6469.