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ARTICLE TYPE

A New Organo–inorganic Hybrid of Poly(cyclotriphosphazene–4,4'bipyridinium) chloride with a Large Electrochromic Contrast

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Supporting Information

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ¹H NMR spectra were recorded on a Bruker Avance 400 ¹⁰ (400 MHz) spectrometer at 295 K in CDCl₃ or DMSO-d6; chemical shifts (δ ppm) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\rm H}$ = 0.00 ppm) or CHCl₃ ($\delta_{\rm H}$ = 7.25 ppm) or ¹⁵ DMSO($\delta_{\rm H}$ = 2.49 ppm). ¹³C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at RT in DMSO-d6; chemical shifts (δ ppm) are reported relative to DMSO-d6 [$\delta_{\rm C}$ = 39.45 ppm (central line). In the ¹H-NMR, the ²⁰ following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet. High-resolution mass spectra (HR-MS) for

material PPBP (**3**) were recorded using Shimadzu Biotech AXIMA Performance (²⁵ MALDI/TOF).



¹H NMR (400 MHz) spectrum of **2** in DMSO-d6

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¹³C NMR (100 MHz) spectrum of PPBP (3) in DMSO-d6



10 ³¹P NMR (162 MHz) spectrum of P₃N₃Cl₆(1) in CDCl₃



³¹P NMR (162 MHz) spectrum of **3** in DMSO-d6



Figure S1 XPS survey spectra of (PNCl₂)₃ trimer and PPBP material.





Figure S2 SEM micrograph and the corresponding EDX plot of the PPBP solid.



Figure S3 TGA of neat IL (EMIB(CN)₄) recorded in the 30–600 $^\circ\text{C}$ temperature range under N₂.

¹⁰ Figure S4 (a) The *in-situ* transmittance spectra of PPBP-PB device recorded under different dc reduction potentials (applied to the blank FTO electrode) in the range of -0.5 to -2.0 V and under different oxidation potentials of +0.5, +1.0 and +1.5 V and (b) the corresponding transmission modulation (Δ T) plots are shown. The device was subjected ¹⁵ to negative potentials starting from -0.5 V and in steps of 0.2 V upto -1.1 V and then in steps of 0.1 V upto -2.0 V. The maximum transmission modulation Δ T_{max} (Δ T = T_{bleach}(+1.5 V) - T_{col}), T_{bleach} at +1.5 V and T_{col} at -0.5 to -2 V;) offered by the device was 70.5 % at λ_{max} of 590 nm by using T_{col} at -2 V and it was 68.9 % at 550 nm. The transmittance data ²⁰ recorded under +1.5 V was used as reference for all Δ T plots.



Figure S5 The ability of the PPBP salt to form radical cations by chemical ²⁵ reduction by using Zn powder and a deep blue color was obtained in solution phase.

5	Table S1 Electrochemical impedance spectroscopy results for PPBP-PB
	device, obtained by fitting the experimental data in the models shown in
	Figure 8.

Applied E / V	R_{CT}/Ω	C_{dl} / μF	Υ₀ / μS
0	390	0.52	-
+0.5	300	0.54	_
+1.0	121	0.56	_
+1.5	44	0.48	_
-0.5	157	1.42	193
-1.0	31	0.68	201
-1.5	14	0.22	2360
-2.0	3.5	1.4	3030