Supplementary Information (SI) for Journal of Materials Chemistry C.

Electronics Supplementary Information

Unveiling mechanical, optical and conductivity properties in naphthalenediimide bridged polysilsesquioxane gels

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Table of Contents

SI-1. Experimental Procedures and Characterizations

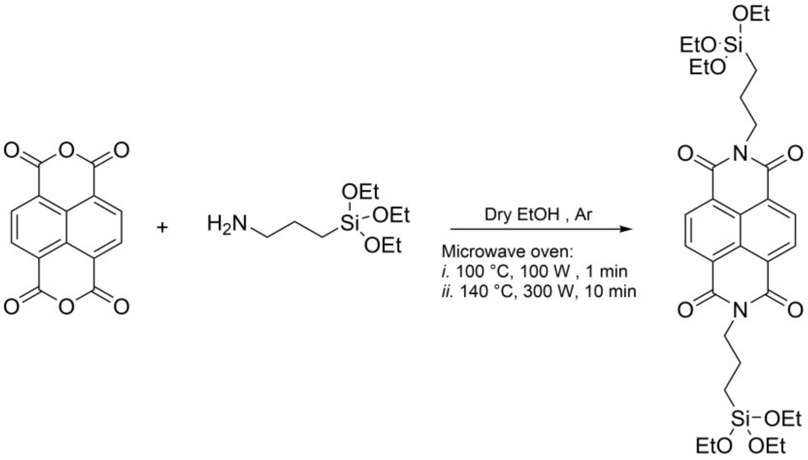
1.1 Synthesis of N,N'-(bis)propyltriethoxysilane-1,4,5,8-tretracarboxylic naphthalene diimide (NDI-PTES):

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.75 (s, 4H, Ar), 4.19 (t, 4H, N-CH_2), 3.83 (q, 12H, O-CH_2), 1.86 (m, 4H, -CH_2-), 1.22 (t, 18H, -CH_3), 0.75 (t, 4H, CH_2-Si).

^{13}C NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 162.89 (4C, C=O); 131 (6C, Ar); 126.75 (4C, Ar); 58.56 (6C, O-CH2); 43.42 (2C, N-CH_2); 21.67 (2C, -CH_2-); 18.40 (6C, CH_3); 8.15 (2C, CH_2-Si)

^{29}Si NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): − 46.24

Yield: 77 %



Scheme ESI1. Chemical synthesis of NDI-PTES.

SI-2. NMR Spectra

The ^{1}H NMR spectrum of **NDI–PTES** in CDCl$_3$ is presented in Figure SI 1. The diagnostic singlet at δ = 8.75 ppm corresponds to the four equivalent aromatic protons of the naphthalene core. The signals for the six ethoxy substituents from the siloxane precursors appear as a triplet at 1.22 ppm (18H, O–*CH*$_2$–CH$_3$) and a quartet at 3.83 ppm (12H, O–CH$_2$–*CH*$_3$). The propyl linkers are clearly identified by the characteristic signals for the three distinct methylene groups: a triplet at 4.19 ppm (4H, N–CH$_2$), a multiplet at 1.86 ppm (4H, N–CH$_2$–CH$_2$*), and a triplet at 0.75 ppm (4H, CH$_2$–Si).[1,2]

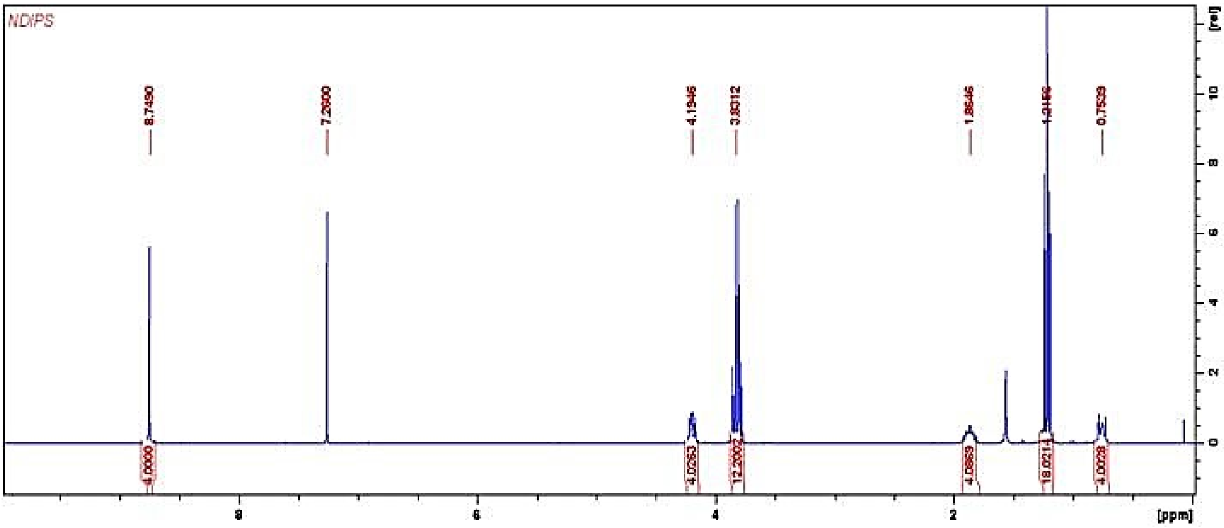


Figure SI 1-^{1}H NMR spectrum of NDI-PTES (CDCl$_3$, 300 MHz, 298 K).

The ^{13}C NMR spectrum (Figure SI 2) further confirms the structure. The aromatic carbons of the naphthalene diimide core resonate at 131.0 and 126.7 ppm (C–H), while the carbonyl carbons give a signal at 162.9 ppm. The propyl chain carbons are observed at 43.42 ppm (N–CH$_2$), 21.67 ppm (N–CH$_2$–CH$_2$), and 8.15 ppm (CH$_2$–Si). The ethoxy substituents resonate at 58.56 ppm (O–CH$_2$) and 18.40 ppm (O–CH$_2$–CH$_3$).[1,2]

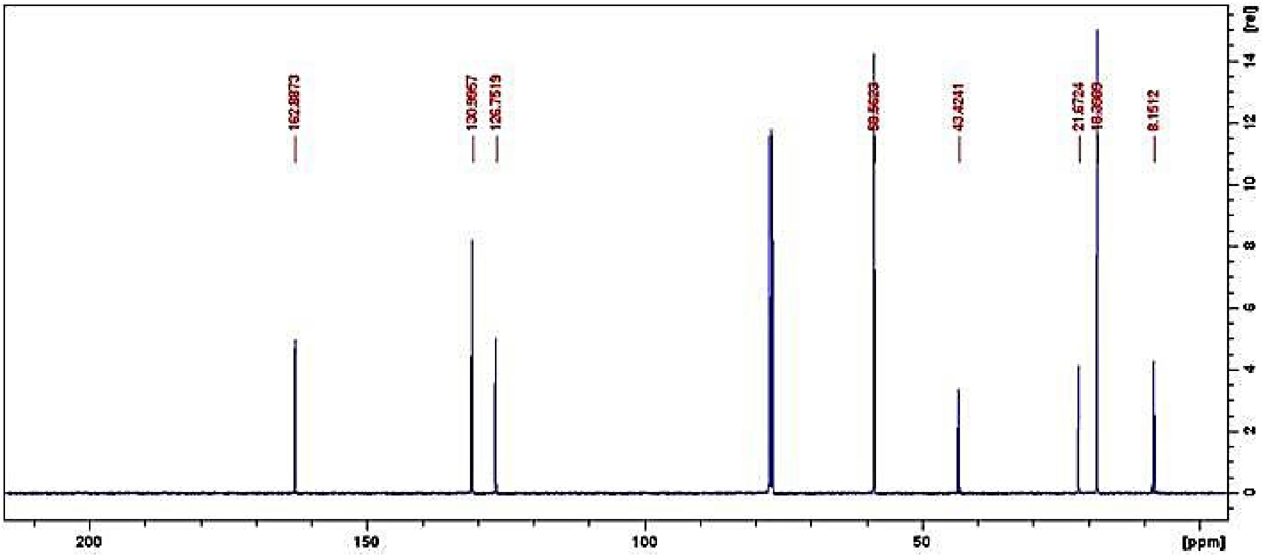


Figure SI 2 - ^{13}C NMR spectrum of NDI-PTES ($CDCl_3$, 400 MHz, 298 K).

^{29}Si NMR spectrum exhibits a single sharp resonance at −46.23 ppm (Figure SI 3). This signal is characteristic of the T^0 substructure, corresponding to the $Si(OEt)_3$ moiety, and indicates the absence of siloxane condensation at this stage.[3]

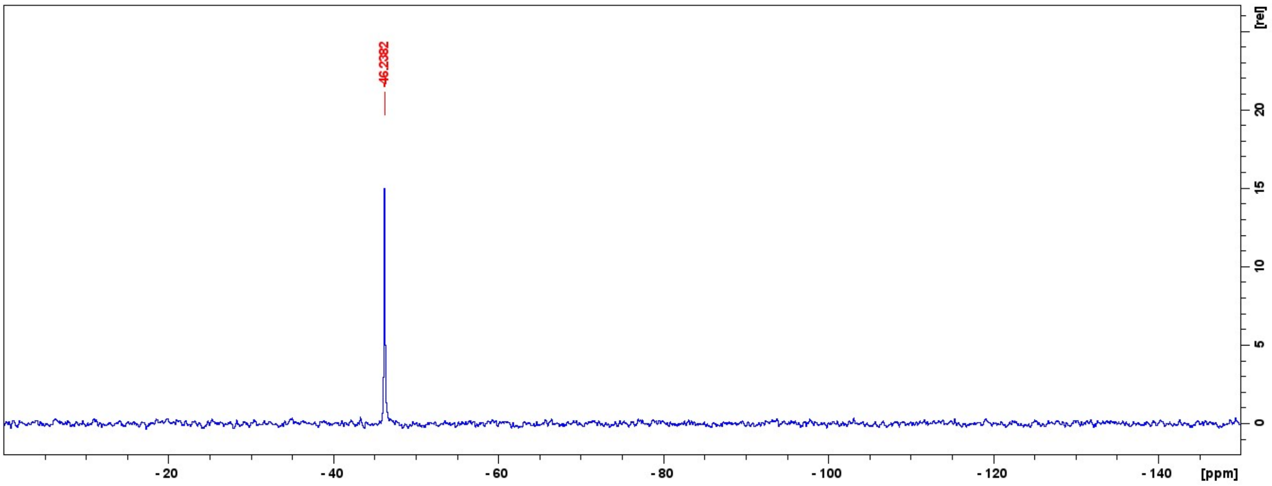


Figure SI 3 - ^{29}Si NMR of NDI-PTES ($CDCl_3$, 400 MHz, 298 K).

SI 3– Infrared spectroscopy

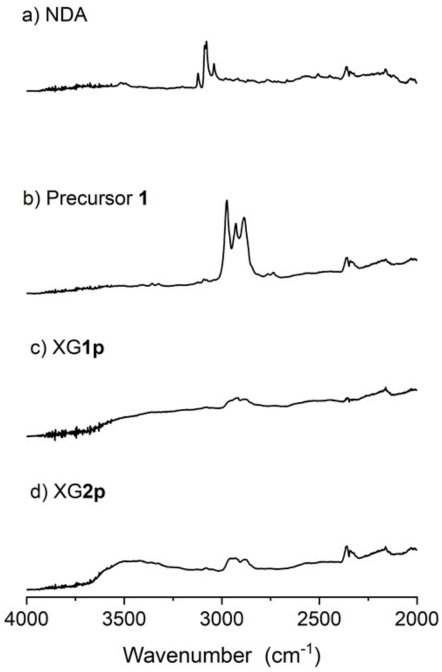


Figure SI 4 - IR-ATR spectra of a) Naphthalene dianhydride (NDA), b) Precursor 1 (NDI-PTES), c) XG1p and d) XG2p.

SI 4 - Luminescence spectrocopy

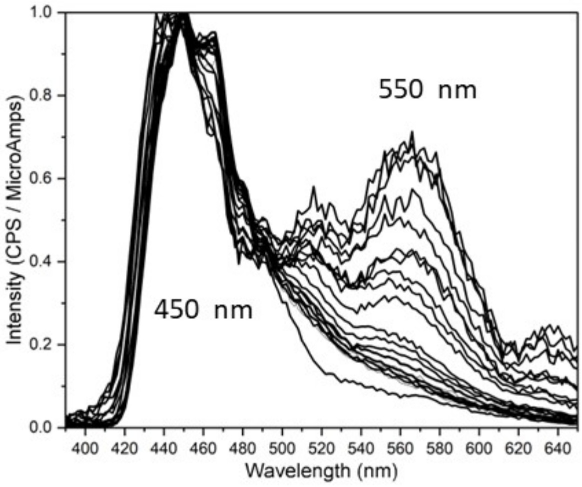


Figure SI 5 – Normalized emission spectra recorded during sol-gel transition of G2p (0.1 M NDI-PS in DMF (+0.1 M HCl at 70 °C) at λ_{exc}= 365 nm. Optical path = 5 mm. fluorimeter set up = frontal mode.

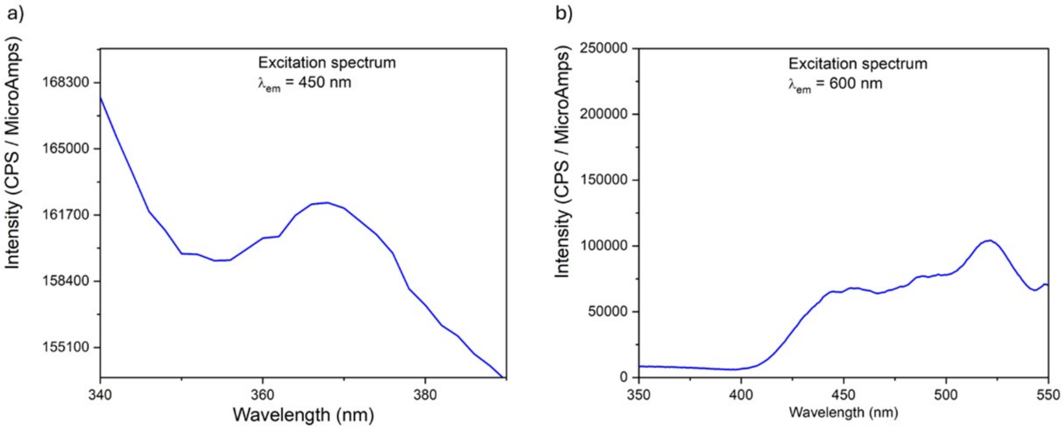


Figure SI 6 – Excitation spectra of gel G2p at (a) l_{em}= 450 nm and (b) l_{em}= 600nm. Measurements were recorded at 25 °C, optical path = 5 mm, fluorimeter set up = frontal mode.

SI 5 - X-Ray Diffractometry

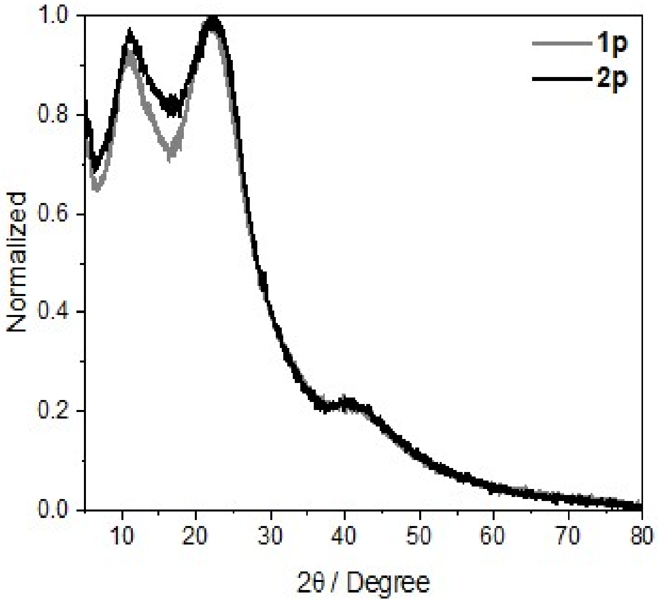


Figure SI 7 - X-ray Powder diffractogram recorded for XG1p and XG2p.

SI 6- Electrochemistry

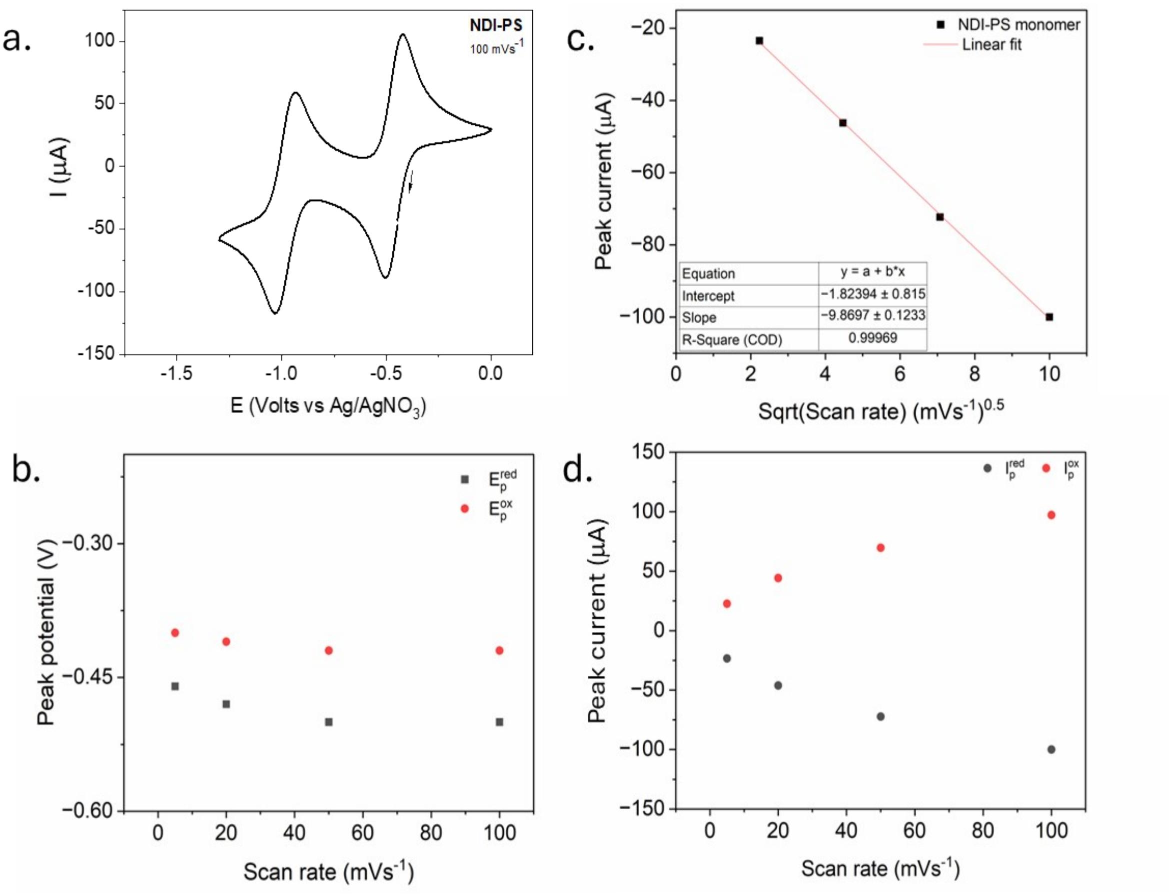


Figure SI 8 - Cyclic voltammetry curves recorded for (a) a 1 mM solution of NDI-PTES in DMF (+ 0.1 M TBAClO$_4$); (b) reduction and oxidation peak potential versus scan rate; (c) reduction peak current versus square root of scan rate; and (d) reduction and oxidation peak current versus scan rate. (Exp. Details: WE=ITO, CE=Pt wire, RE= Ag/AgNO$_3$, start potential = OCP).

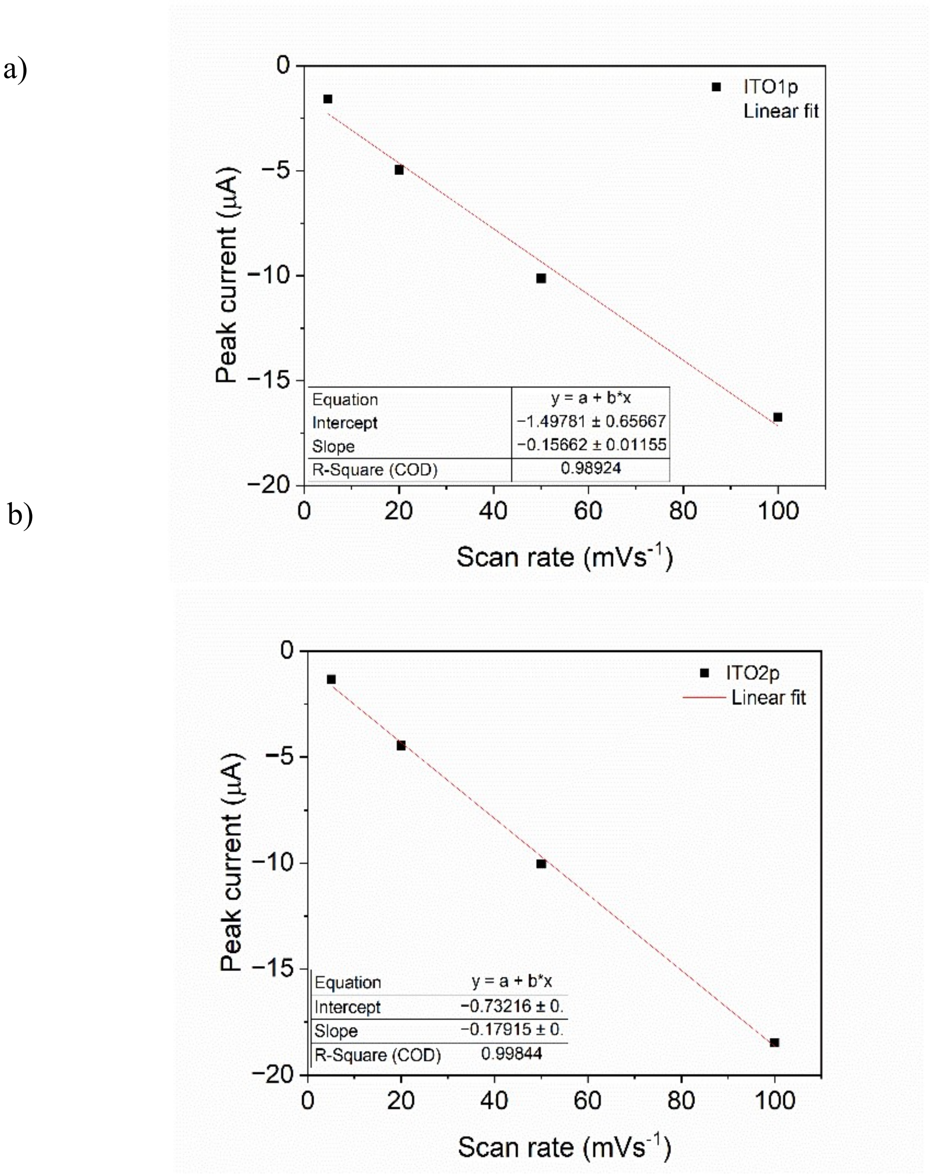


Figure SI 9 - Linear relationship between reduction peak current and scan rate from (a) ITO1p and (b) ITO2p modified electrodes in DMF (+0.1 $TBAPF_6$). (WE=ITO; CE=Pt wire, RE=Ag/AgNO3, Scan rate= 5 mVs-1, starting potential = OCP).

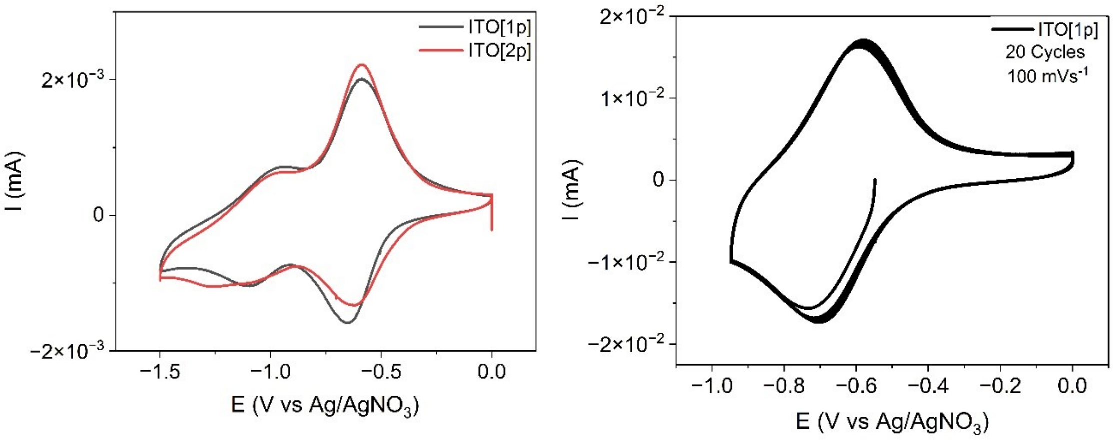


Figure SI 10 – Electrochemical characterization of ITO**1p** and ITO**2p** films. (a) Comparative cyclic voltammograms of ITO**1p** (black) and ITO**2p** (red) recorded in DMF with 0.1 M $TBAPF_6$ at 5 $mV{\cdot}s^{-1}$. (b) Stability assessment: first reduction process of the ITO**1p** electrode over 20 consecutive cycles at 100 mVs^{-1}, demonstrating electrochemical robustness. *Experimental conditions:* Working electrode (WE) = ITO; counter electrode (CE) = Pt wire; reference electrode (RE) = $Ag/AgNO_3$ (0.01 M in ACN); initial potential = open-circuit potential (OCP).

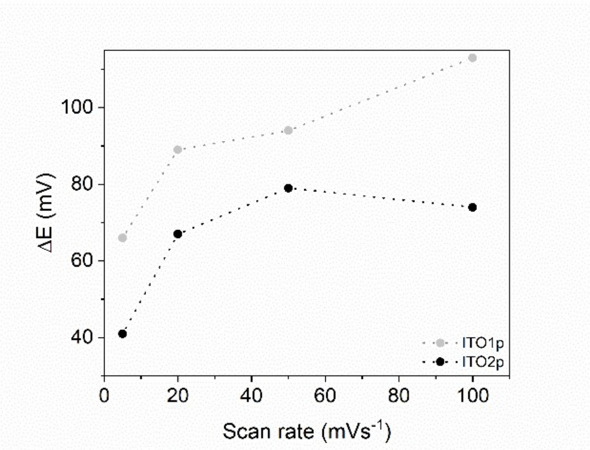


Figure SI 11 - Peak-to-peak potential (ΔE_p) measured for ITO1p and ITO2p at varying scan rates. (WE=ITO, CE:Pt, RE=$Ag/AgNO_3$, 0.1 M $TBAClO_4$ in DMF).

SI 7- Spectroeletrochemistry

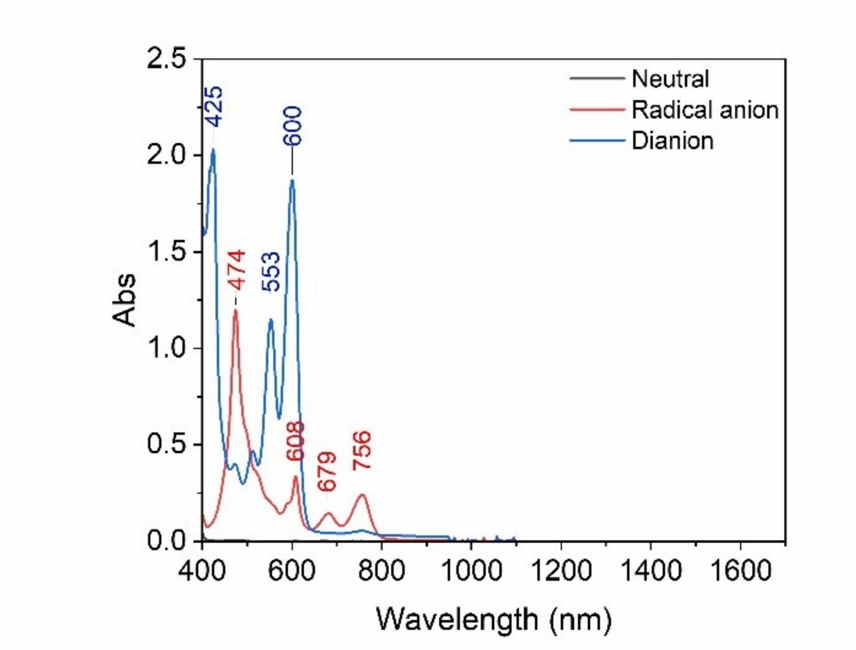


Figure SI 12 - Absorption spectra recorded during the potentiostatic reduction of 10 mL solution of NDI-PTES (10^{-4} M) in DMF (+0.1 M TBATFSI),(WE= carbon , CE= Pt wire and RE= Ag/AgNO3) recorded with 1mm UV-vis probe).

SI 8- UV-vis absorbance

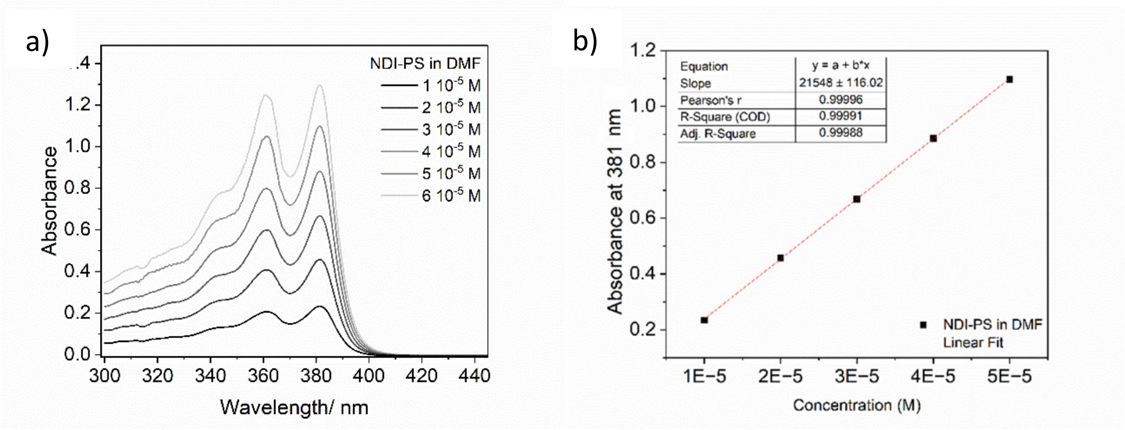


Figure SI 13 - (a) UV-Vis absorption spectra of NDI-PTES in DMF at varying concentrations. (b) Linear dependence (Lambert-Beer law) of the absorbance at 381 nm as a function of concentration, measured in 1 cm quartz cuvettes.

References

1 G. M. Prentice, L. M. Emmett, H. Zhu, G. Kociok-Köhn and G. D. Pantoş, *Supramol Chem*, 2016, 28, 161–167.

2 B. Castanheira, E. R. Triboni, L. D. S. Andrade, F. D. J. Trindade, L. Otubo, A. C. S. C. Teixeira, S. Brochsztain, *Langmuir*, 2018, 34(28), 8195-8204.

3 H. Sardon, L. Irusta, M. J. Fernández-Berridi, M. Lansalot, E. Bourgeat-Lami, *Polymer*, 2010, 51(22), 5051-5057.