Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Get closer to the intrinsic properties of Ni^{2+}salen polymer semiconductors accessed by chain isolation inside silica nanochannels

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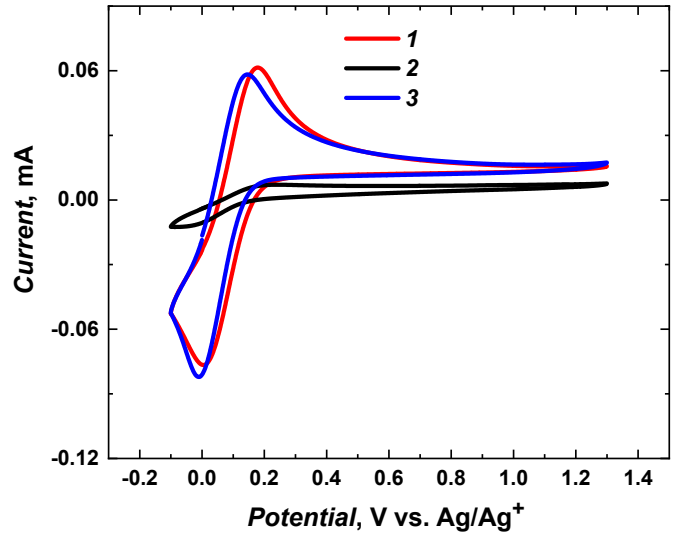

Fig. S1 CV curves registered at 20 mVs^{-1} in the propylene carbonate solution containing 1 mM bis(pentamethylcyclopentadienyl)iron and 0.1 M $TBAPF_6$ at (*1*) the bare ITO electrode, (*2*) the ITO electrode coated with mesoporous silica channels filed with CTAB (before CTAB extraction), and (*3*) the ITO electrode coated with open channels of mesoporous silica matrix (after CTAB extraction).

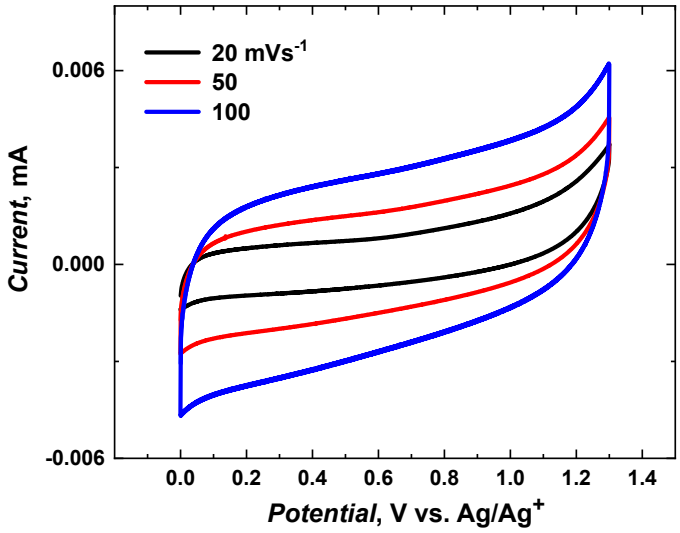

Fig. S2 CV curves registered for the ITO electrode coated with open channels of mesoporous silica matrix (after CTAB extraction) in 0.1 M $(TBA)PF_6$, in propylene carbonate at different potential scan rates.

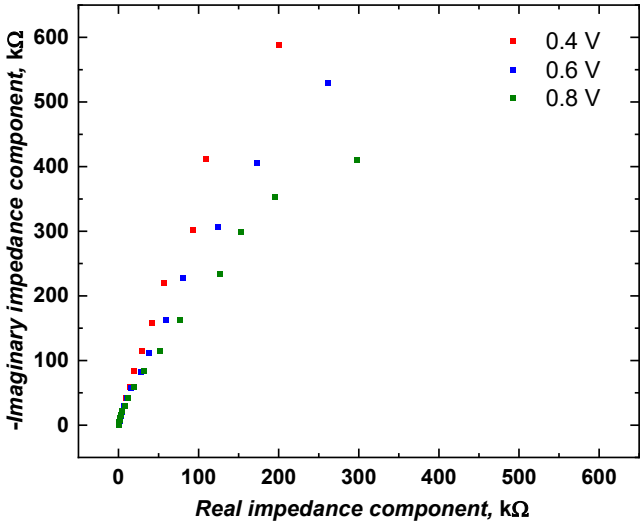

Fig. S3 Nyquist plots for the ITO electrode coated with open channels of mesoporous silica matrix (after CTAB extraction)at different applied potentials (a) 0.4 V, (b) 0.6 V and (c) 0.8 V in 0.1 M (TBA)PF_6, in propylene carbonate. Before the EIS measurements, the electrode was equilibrated at selected potential for 30 s. After that time, the current reached equilibrium, and then EIS measurements were performed with the voltage amplitude of 10 mV in the frequency range of 100 kHz to10 mHz.

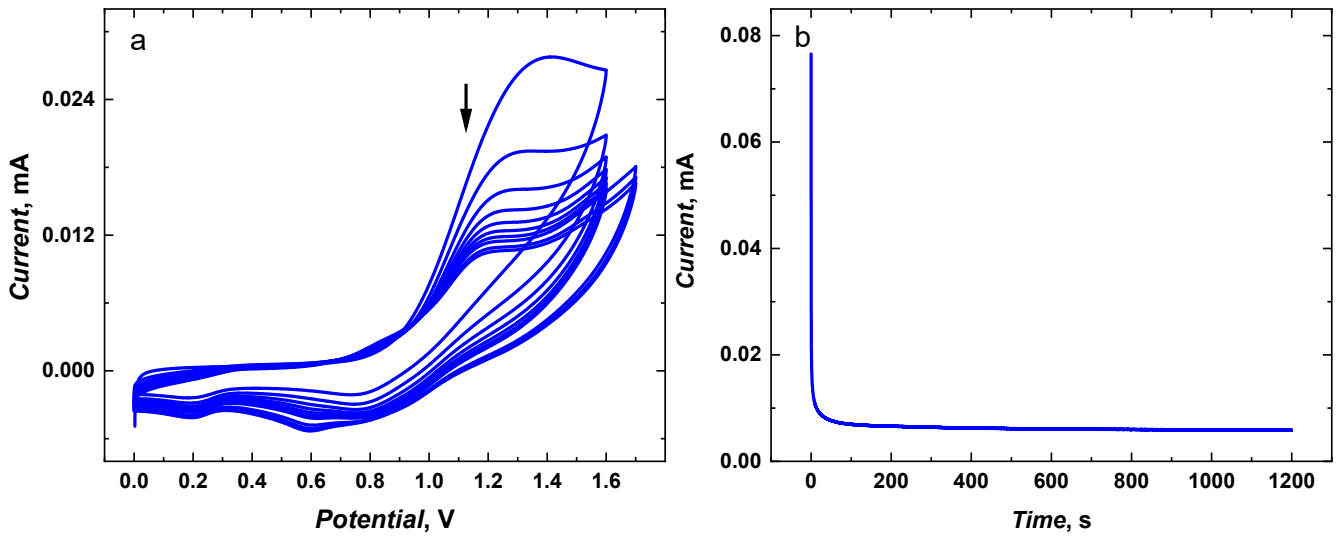
a
0.024
0.012
0.000
Current, mA
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Potential, V
b
0.08
0.06
0.04
0.02
0.00
Current, mA
0
200
400
600
800
1000
1200
Time, s

Fig. S4 (a) Multicyclic potentiodynamic curves of the oxidative electropolymerization attempt of 0.5 mM *meso*-NiSaldMe on the ITO electrode coated with open channels of mesoporous silica matrix in a propylene carbonate solution of 0.1 M (TBA)PF_6. A potential scan rate was 100 mV s^{-1}. (b) The potentiostatic curve recorded during the electropolymerization attempt of 0.5 mM poly(NiSaltMe) on the ITO electrode coated with open channels of mesoporous silica matrix in a propylene carbonate solution of 0.1 M (TBA)PF_6, at 1.60 V vs. Ag/Ag^+.

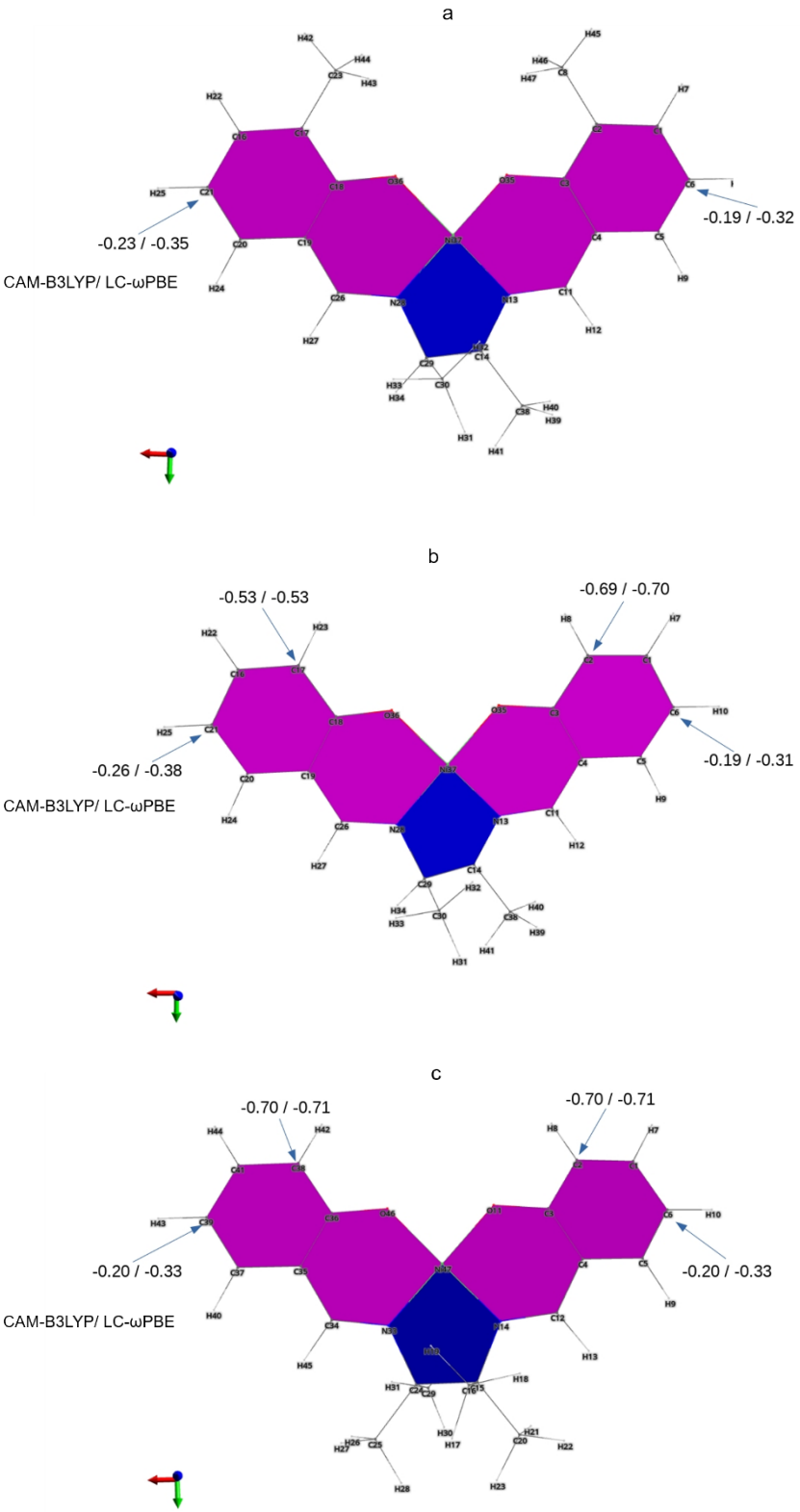

Fig. S5 The values of Mulliken charges determined from DFT optimized monomer structures of (a) *meso*-NiSaldMe-3dMe), (b) *meso*-NiSaldMe), and (c) NiSaltMe.

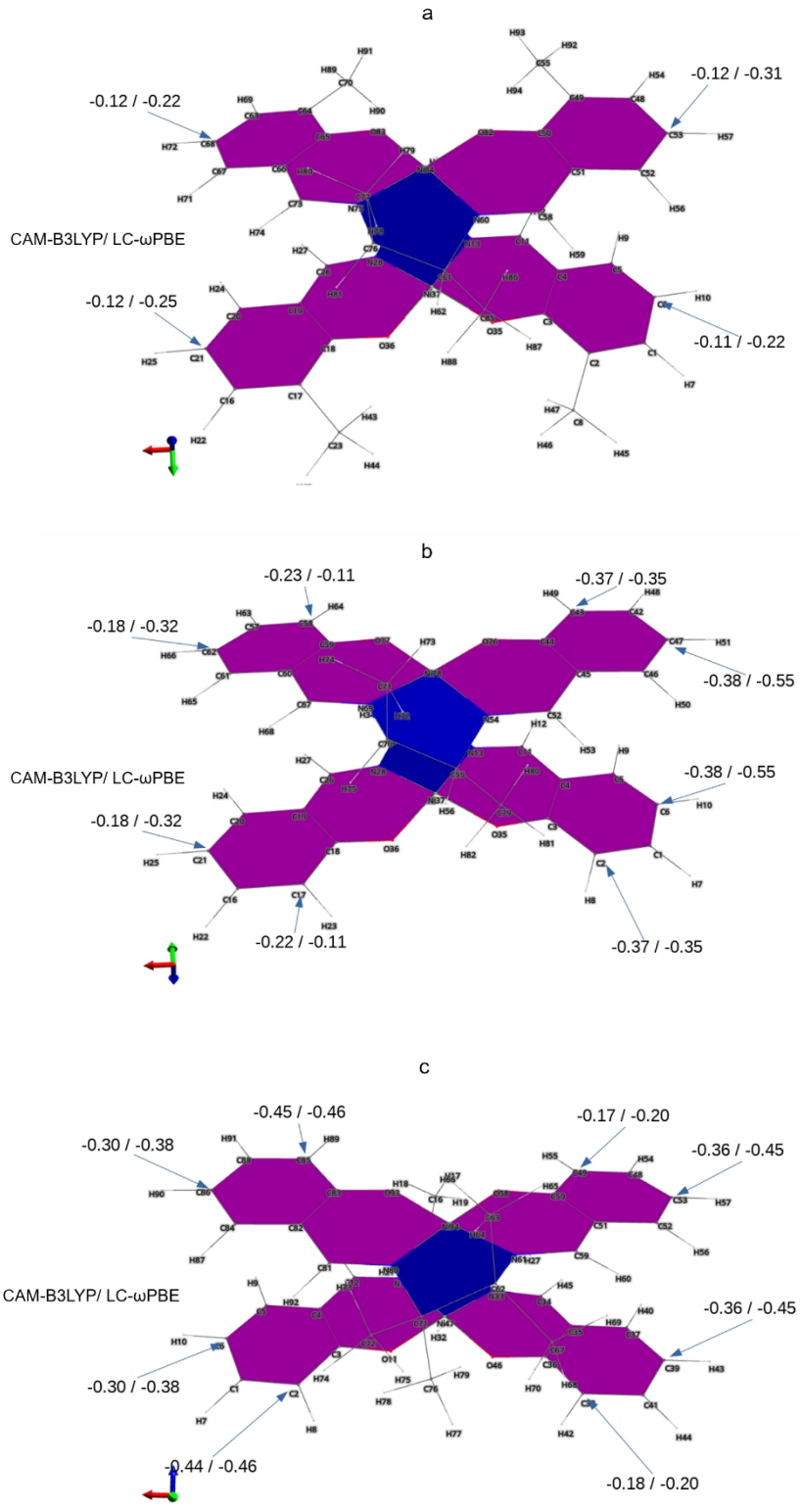

Fig. S6 The values of Mulliken charges determined from DFT optimized anti-parallel π-π stacked dimer structures of (a) *meso*-NiSaldMe-3dMe, (b) *meso*-NiSaldMe), and (c) NiSaltMe.

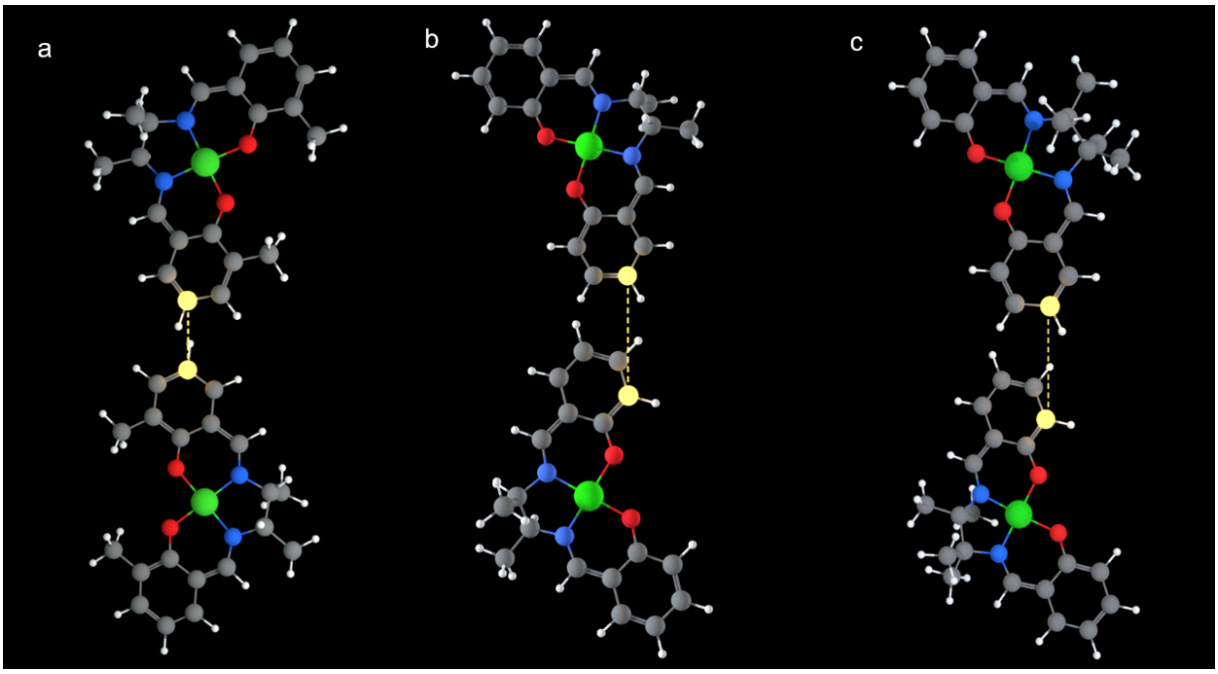

Fig. S7 The bonding placement between anti-parallel polymer units for (a) *meso*-NiSaldMe-3dMe, (b) *meso*-NiSaldMe), and (c) NiSaltMe.

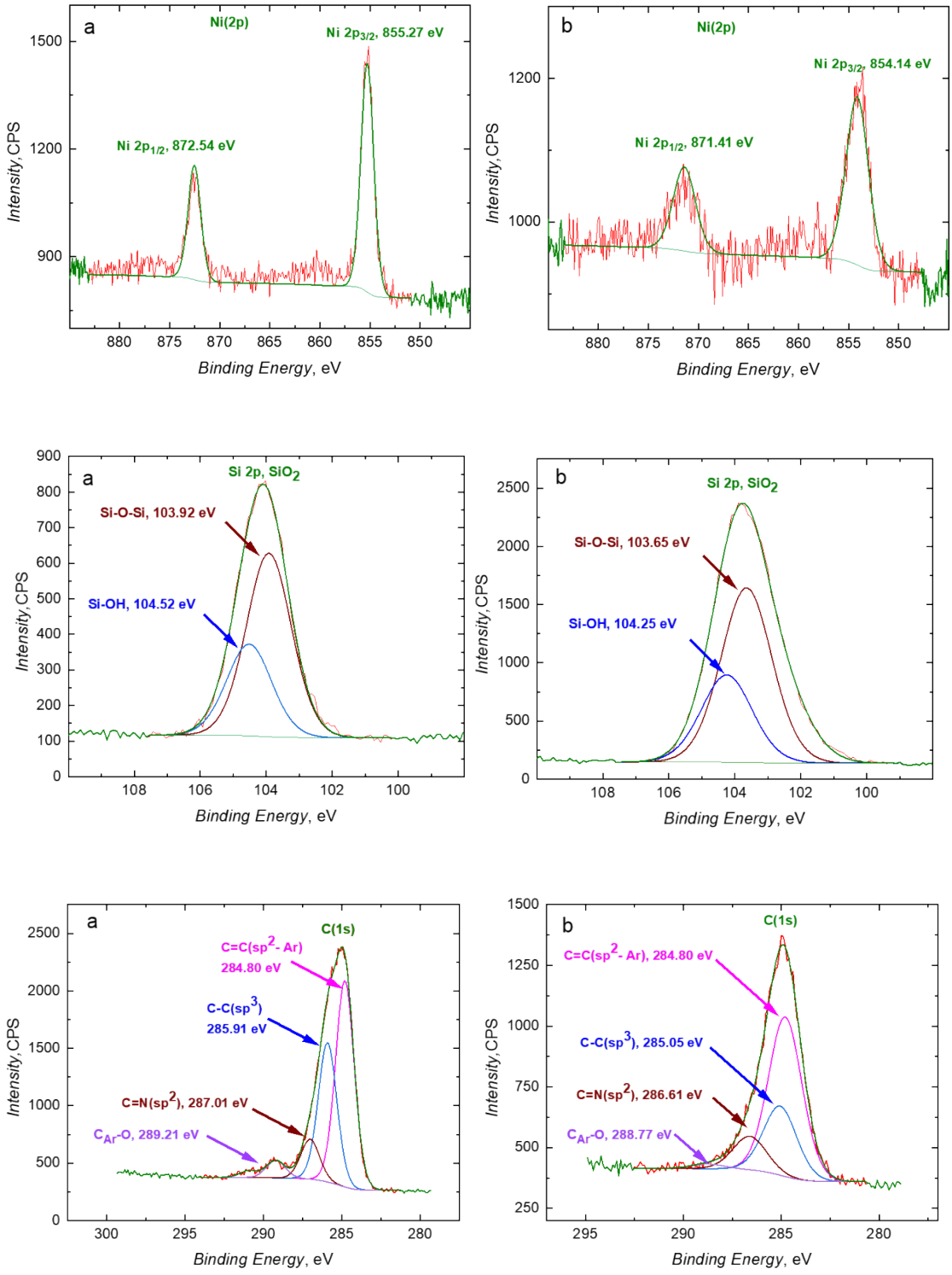

Fig. S8 XPS spectra obtained for poly(*meso*-NiSaldMe-3dMe) molecular wires deposited inside mesoporous silica channels, respectively (a) before, and (b) after the low energy argon ion beam sputtering conducted by 16 min (500 V, 2×2 mm, sputter rate: 1.12 nm/min). Notably, obtained Ni(2p) photoelectron spectra are characteristic of the square-planar Ni^{2+} geometry in preserved in poly(*meso*-NiSaldMe-3dMe) molecular wires. The small changes observed on the baseline level in the 1C (s) spectrum registered before the low-energy argon

ion beam sputtering at 280 - 290 eV are caused by CO_2 adsorption/contamination from the air.[1, 2]

Reference

1. J. F. Moulder and J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, Physical Electronics Division, Perkin-Elmer Corporation, 1992.
2. S. Yamamoto, K. Takeuchi, Y. Hamamoto, R.-Y. Liu, Y. Shiozawa, T. Koitaya, T. Someya, K. Tashima, H. Fukidome, K. Mukai, S. Yoshimoto, M. Suemitsu, Y. Morikawa, J. Yoshinobu and I. Matsuda, *Physical Chemistry Chemical Physics*, 2018, **20**, 19532-19538.