

Supporting Information

Organization and intramolecular charge-transfer enhancement in tripodal tris[(pyridine-4-yl)phenyl]amine push-pull molecule by intercalation into layered materials bearing acidic functionalities

Klára Melánová,^a Daniel Cvejn^b, Filip Bureš,^b Vítězslav Zima,^{a*} Jan Svoboda,^a Ludvík Beneš,^c
Tomáš Mikysek,^d Oldřich Pytela,^b Petr Knotek^c

^a *Institute of Macromolecular Chemistry, AS CR, Heyrovsky sq. 2, 162 06 Prague 6, Czech Republic*

^b *Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic*

^c *Joint Laboratory of Solid State Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic*

^d *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic*

General: Column chromatography was carried out with silica gel 60 (particle size 0.040-0.063 mm, 230-400 mesh) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 360 nm). Melting points (m.p.) were measured in open capillaries and were uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz at 25 °C with a Bruker AVANCE III 400 instrument. Chemical shifts are reported in ppm relative to the signal of Me_4Si . The residual solvent signal in the ^1H and ^{13}C NMR spectra was used as an internal reference (DMSO- d_6 2.55 and 39.51 ppm). Apparent resonance multiplicities are described as s (singlet) and d (doublet). ^1H signals of 1,4-phenylene/pyridine-4-yl moieties were denoted as Ph/Py. IR spectra were recorded as neat using HATR adapter on a Perkin-Elmer FTIR Spectrum BX spectrometer. High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (m/z 50 - 1500) with the following setting of tuning parameters: resolution 100,000 at $m/z = 400$, laser energy 17 mJ, number of laser shots 5, respectively. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width $\Delta m/z$ 4, normalized collision energy 25%, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for CID experiments in LTQ linear ion trap. Mass spectra were averaged over the whole MS record (30 s) for all measured samples. UV/Vis spectra of **TPPA** and **MeTPPA** were recorded on a HP 8453 spectrophotometer in CH_3OH ($c = 2 \times 10^{-5}$ M). The normalized DR-UV Vis spectra were deconvoluted using the OriginPro 6.1 software (OriginLab Corp., USA) by energy symmetric functions (Gaussian bands). The maxima of the bands are located at the wavelength 450 and 370 nm for

protonated and deprotonated form of **TPPA**, respectively. The ratio of the areas protonated to the deprotonated **TPPA** bands are 0.29 and 0.15 for **ZrSPP** and **ZrP** guests, respectively.

Preparation of TPPA. A mixture of tris(4-iodophenyl)amine (1.01 g, 1.62 mmol) and pyridine-4-ylboronic acid (717 mg, 5.84 mmol) in dioxane (40 ml) and water (20 ml) was placed in dried Schlenk flask. Argon was bubbled through the solution whereupon [Pd(PPh₃)₄] (187 mg, 0.16 mmol) and Na₂CO₃ (650 mg, 6.13 mmol) were added and the reaction was stirred at 91 °C for 16 h. The reaction was cooled to 25 °C, diluted with water and extracted with CH₂Cl₂ (2 × 250 ml). Combined organic extracts were dried (Na₂SO₄), the solvents were evaporated *in vacuo* and the residue was purified by column chromatography (SiO₂; EtOAc/MeOH 4:1) to afford 700 mg (91 %) of **TPPA** as a yellowish solid. Spectral characterization is similar to that reported in literature.^{6,7}

Preparation of MeTPPA. A mixture **TPPA** (150 mg, 0.31 mmol) and CH₃I (15 ml, 0.24 mol) was stirred at 25 °C. The reaction mixture turned orange within 5 min and reddish precipitate began to appear. The remaining CH₃I was evaporated *in vacuo* after 2 h of stirring to afford 279 mg (99 %) of MeTPPA as a reddish solid. M.p. 156-157 °C. ¹H-NMR (DMSO-*d*₆, 400 MHz, 25 °C): δ = 4.37 (9H, s, 3 × CH₃), 7.41 (6H, d, *J* = 8.7 Hz, 3 × Ph), 8.20 (6H, d, *J* = 8.7 Hz, 3 × Ph), 8.53 (6H, d, *J* = 6.8 Hz, 3 × Py), 9.02 (6H, d, *J* = 6.8 Hz, 3 × Py). ¹³C-NMR (DMSO-*d*₆, 100 MHz, 25 °C): δ = 46.99, 123.31, 124.95, 128.82, 129.93, 145.47, 149.01, 153.03. HR-MALDI-MS *m/z*: 521.2701 ([M-3I]⁺), C₃₆H₃₃N₄⁺ requires 521.2700.

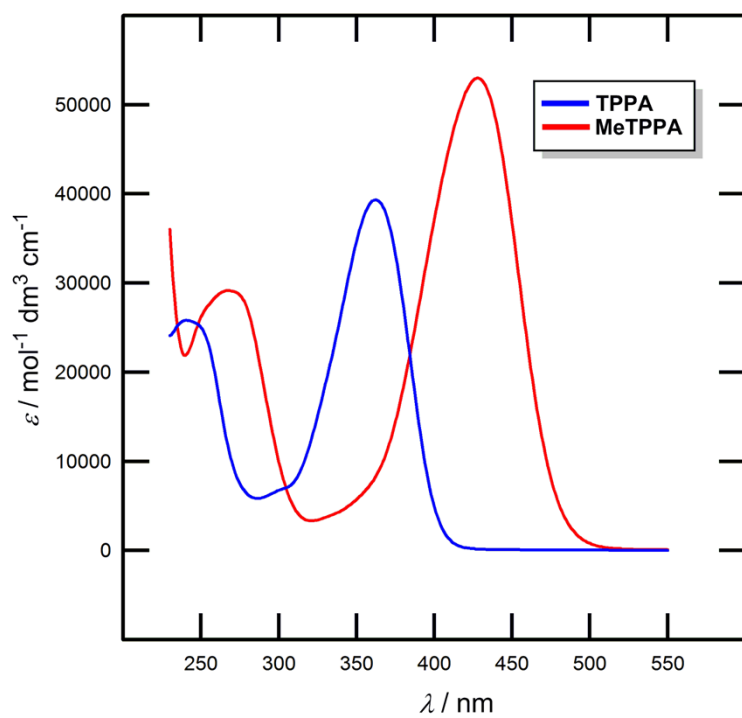


Figure S1 UV-Vis absorption spectra of **TPPA** and **MeTPPA** measured in CH_3OH ($c = 2 \times 10^{-5} \text{ M}$).

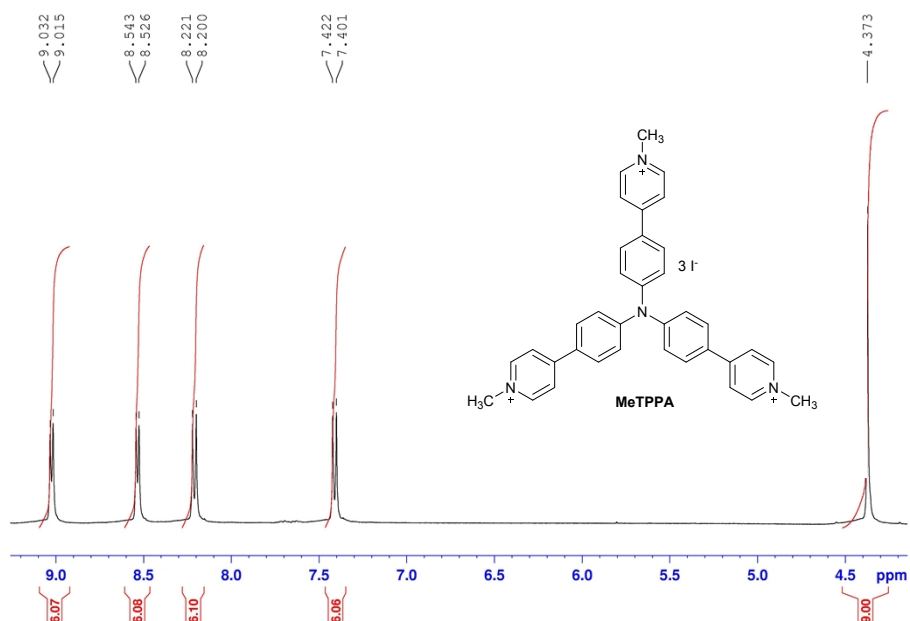


Figure S2 ^1H NMR spectrum of **MeTPPA** (DMSO, 400 MHz, 25 °C).

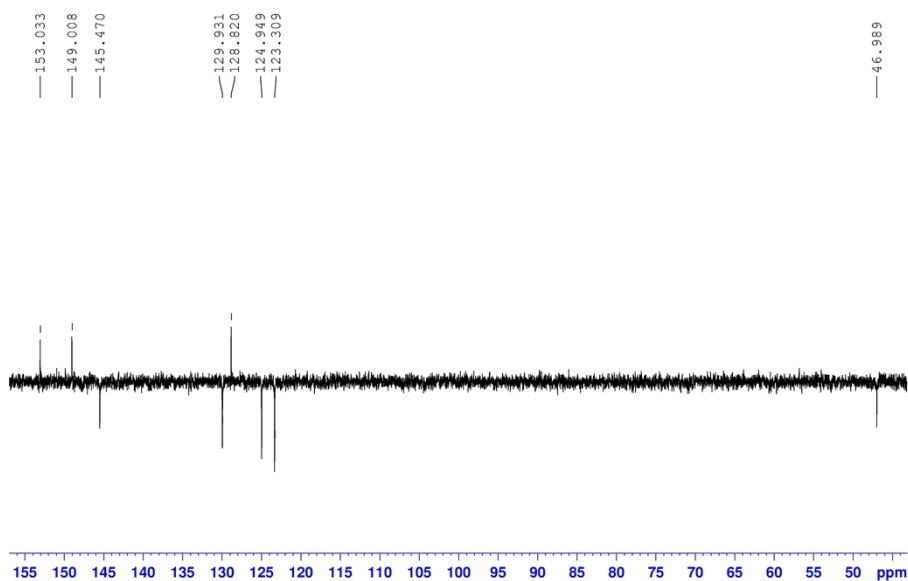


Figure S3 ^{13}C NMR APT spectrum of MeTPPA (DMSO, 100 MHz, 25 °C).

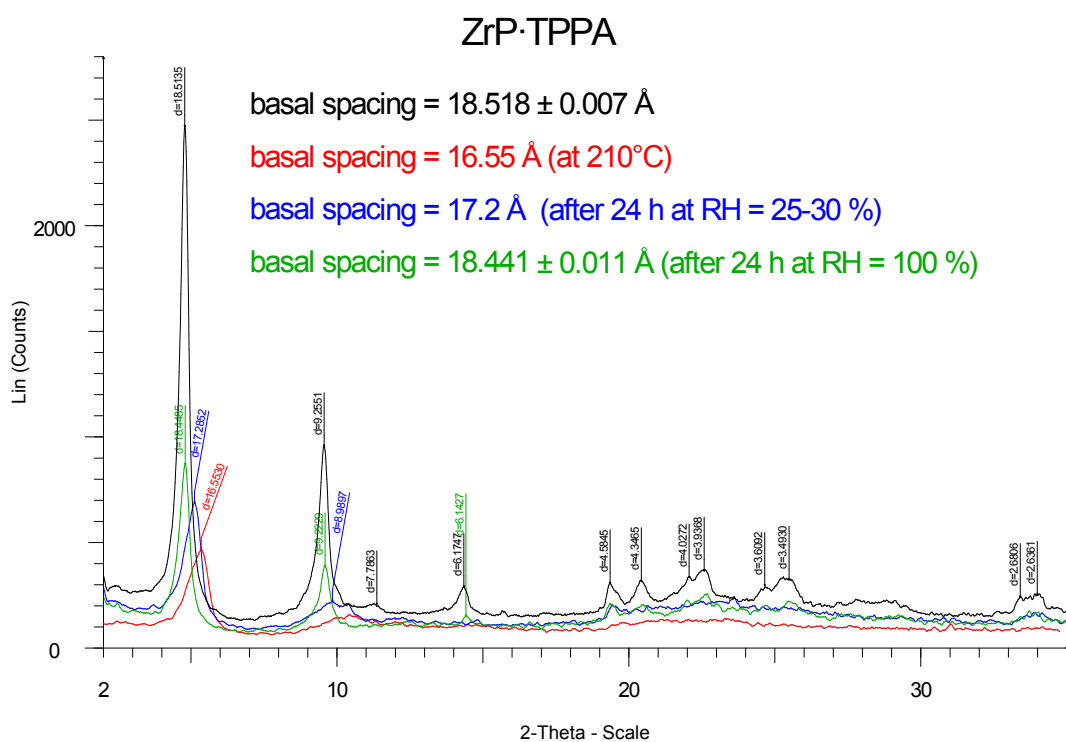


Figure S4 The change of the powder X-ray patterns of ZrP·TPPA on heating to 210°C and subsequent rehydration at 25-30% RH and then at 100% RH at room temperature.

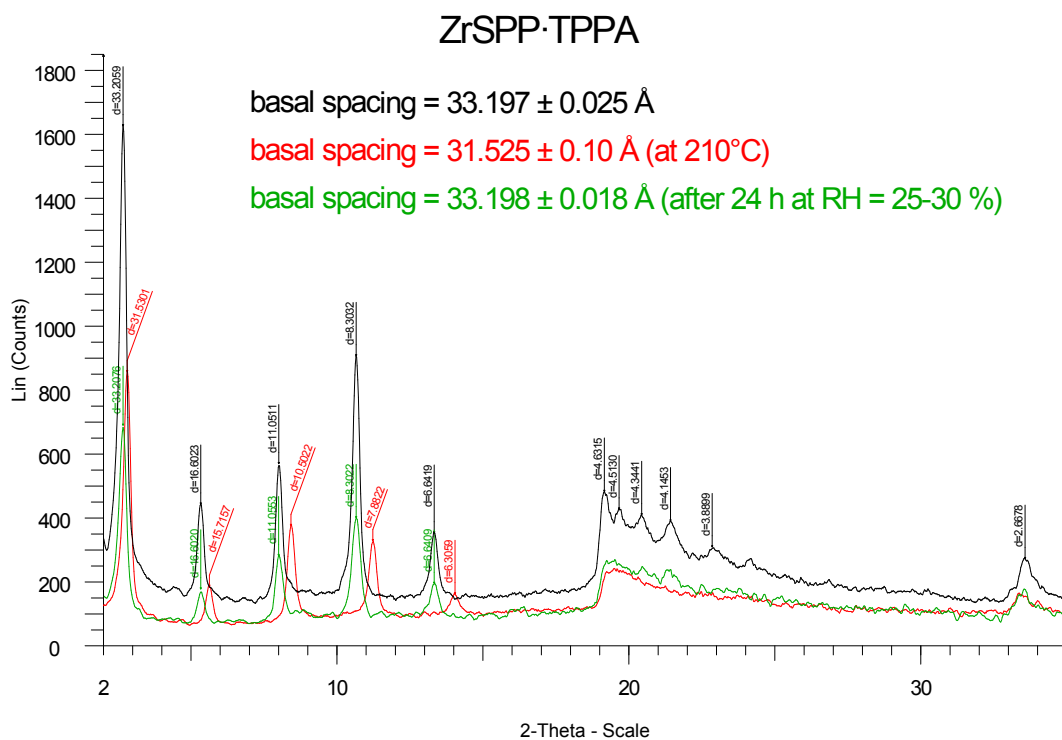


Figure S5 The change of the powder X-ray patterns of **ZrSPP·TPPA** on heating to 210°C and subsequent rehydration at 25-30% RH at room temperature.

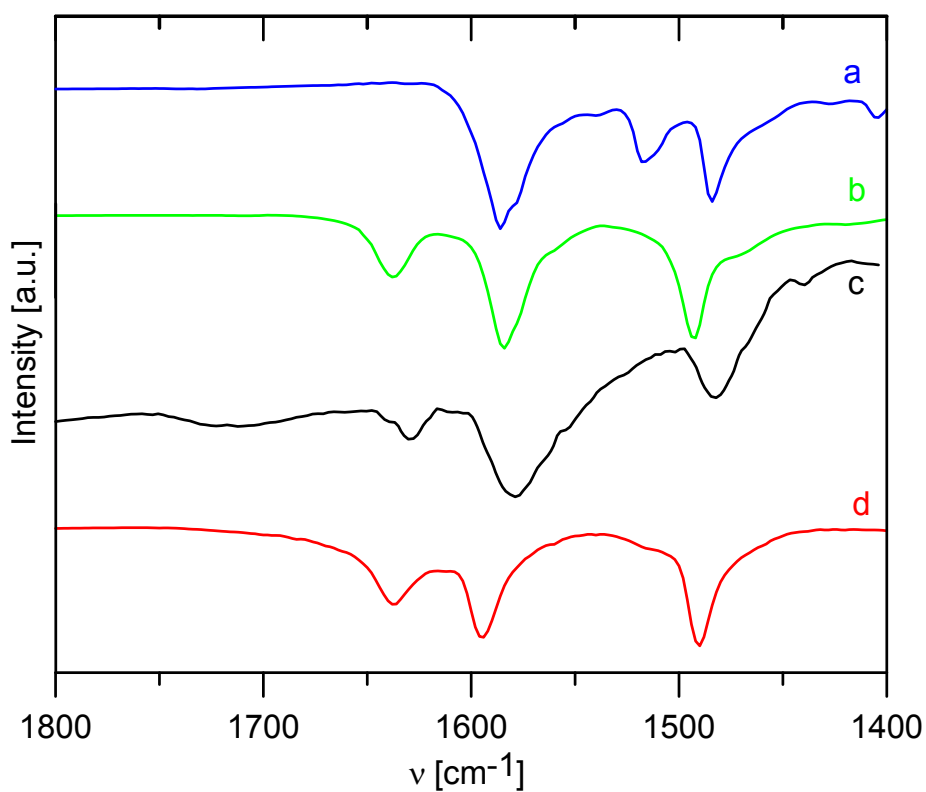


Figure S6 IR spectra of **TPPA** (a), **MeTPPA** (b), **TPPA** protonated with HCl (molar ratio of $\text{TPPA}/\text{HCl} = 1/1.5$) (c), **ZrP·TPPA** (d).

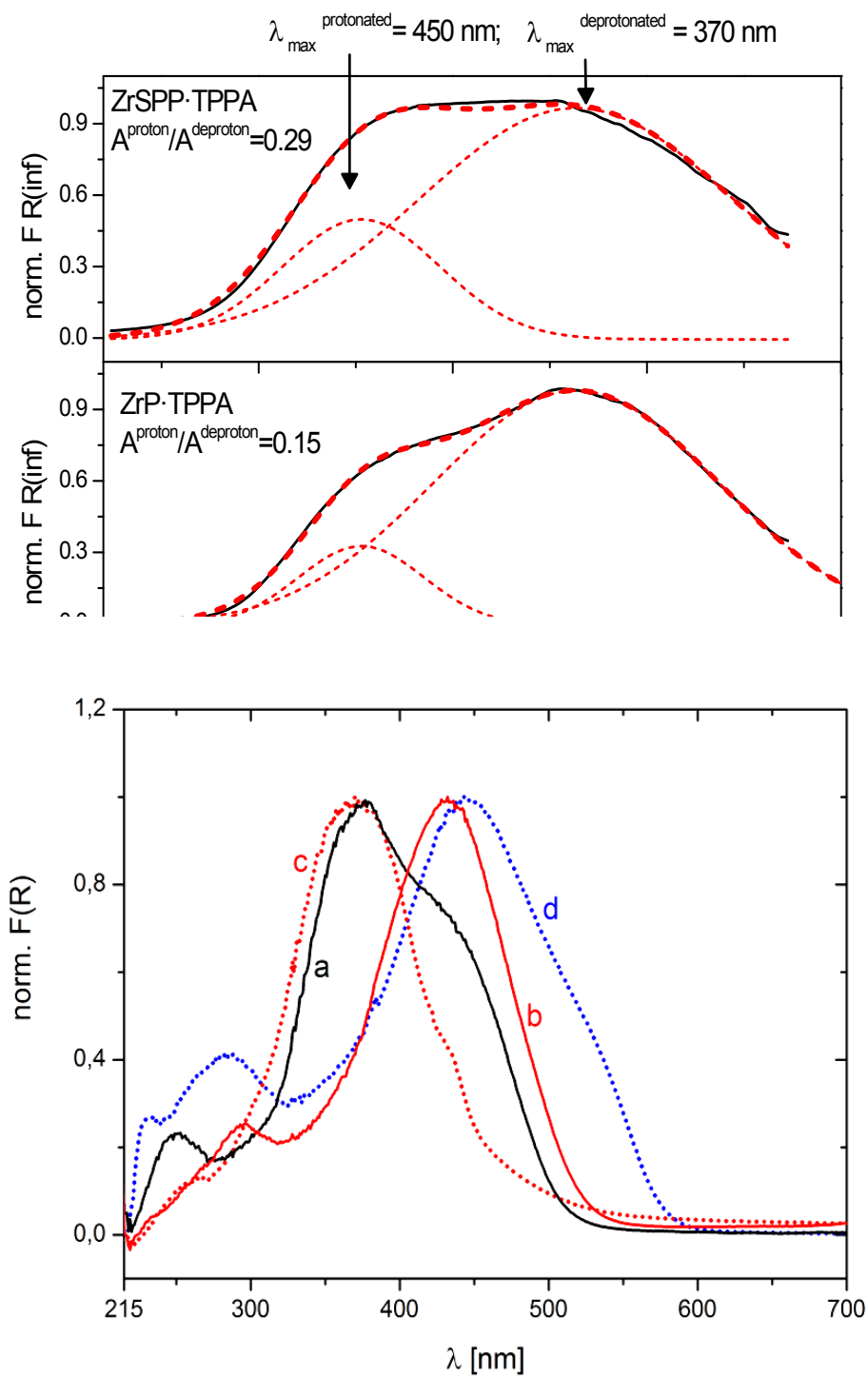


Figure S7 Deconvolution of the UV-Vis spectra of the **ZrP·TPPA** and **ZrSPP·TPPA** intercalates.

Figure S8 UV-Vis spectra of **ZrP·TPPA** (a), **ZrP·TPPA** treated with HCl (b), **TPPA** (c), **MeTPPA** (d).