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

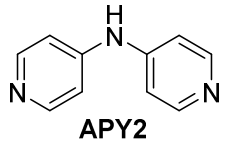
Effect of intercalation and chromophore arrangement on the linear and nonlinear optical properties of model aminopyridine push-pull molecules

Filip Bureš, Daniel Cvejn, Klára Melánová, Ludvík Beneš, Jan Svoboda, Vítězslav Zima, Oldřich Pytela, Tomáš Mikysek, Zdeňka Růžičková, Iwan V. Kityk, Artur Wojciechowski, and Nasser AlZayed

Table of Content

1. Synthesis and characterization of APY2-3 and MeAPY1-3

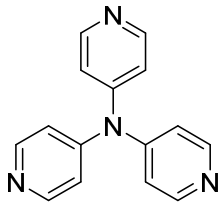
1.1. Di(pyridin-4-yl)amine (APY2)



APY2

The title compound was synthesized via modified literature procedure.[1] To a solution of **APY1** (9.4 g, 0.1 mol) in PCl_3 (9.2 ml, 0.105 mol), pyridine (17.8 ml, 0.22 mol) was added dropwise. The reaction mixture was refluxed at 140 °C for 5 h resulting in a thick orange suspension. All remaining liquids were distilled off and ethanol (5 mL), water (50 mL) and subsequently conc. HCl (10 mL) were slowly added to almost dry residue. The reaction was heated at 105 °C for 1 h, filtered while hot and the filtration cake was washed with HCl (20 %, 2 × 100 mL). The supernatant was cooled to 0 °C and alkalized to pH 9-10 with aq. NaOH (1 M). The formed off-white precipitate was collected by filtration, washed with water (2 × 50 mL) and diethylether (2 × 50 ml). The crude product was purified by a filtration though a short plug (SiO_2; MeOH) or crystalization (EtOH/water 2:1). Pale white solid. Yield 7.6 g (44 %). M. p. 282–284 °C (lit.[2] 273–274 °C). IR (HATR): ν_{max} = 2668, 1574, 1485, 1343, 1205, 831, 998, 798 cm^{-1}. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 °C): δ_H = 7.16 (d, 4H, ^3J = 6.4 Hz, NPy*H*), 8.39 (d, 4H, ^3J = 6.4 Hz, N-Py*H*), 9.39 (brs, 1H, N*H*Py). ^{13}C-NMR (125 MHz, d_6-DMSO, 25 °C): δ_C = 111.7, 147.8, 150.5 ppm. HR-MALDI-MS (DHB): calcd for $C_{10}H_9N_3$ ($[M+H]^+$) 172.08692; found 172.08730.

1.2. Tri(pyridin-4-yl)amine (APY3)



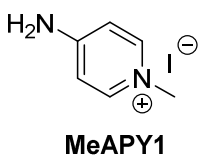
APY3

APY2 (514 mg, 3.0 mmol), 4-iodopyridine (615 mg, 3.0 mmol), CuBr (430 mg, 3.0 mmol) and Cs_2CO_3 (977 mg, 3.0 mmol) were placed to a flame-dried Schlenk flask under argon. Dry NMP (30 mL) was added and argon was bubbled through the reaction mixture for 10 min. The reaction mixture was heated at 190 °C for 8 h, cooled to 25 °C, filtered through a short pad of celite and diluted with water (400 mL). Aq. NH_3 (25–27 %; 50 mL) was added and the resulting mixture was extracted with DCM (3 × 250 mL). The combined extracts were washed with aq. NH_3 (15 %, 100 mL), water (5 × 100 mL), dried (Na_2SO_4) and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (SiO_2; EtOAc/MeOH 10:1). Beige solid. Yield 350 mg (47 %). M. p. 259–261 °C. IR (HATR), ν_{max} = 2926, 1573, 1494, 1290, 822, 622 cm^{-1}. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 °C): δ_H = 7.01 (d, 6H, ^3J = 6 Hz, NPy*H*), 8.52 (d, 6H, ^3J = 6 Hz, NPy*H*). ^{13}C-NMR (125 MHz, d_6-DMSO, 25 °C): δ_C = 118.6, 151.5, 151.7 ppm. HR-MALDI-MS (DHB): calcd for $C_{15}H_{13}N_4$ ($[M+H]^+$) 249.11347; found 249.11410.

1.3. General method for *N*-methylation (MeAPY1-3)

Appropriate aminopyridine **APY1-3** (1 mmol) and iodomethane (14.2 g, 100 mmol) were placed in a flask and were stirred for 8 h. The resulting precipitate was filtered off and was washed with CH_2Cl_2 (3 × 75 mL) to provide **MeAPY1-3** of sufficient purity. However, **MeAPY1-3** can further be recrystallized from propan-2-ol.

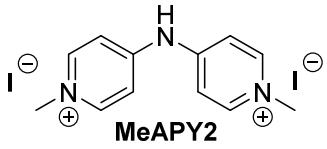
1.4. MeAPY1



MeAPY1

The title compound was prepared from **APY1** (94 mg) White solid. Yield 235 mg (> 99 %). IR (HATR) ν_{max} = 3145, 1651, 1537, 1198, 825, 610 cm^{-1}. M.p. 184–186 °C (lit.[3] 188–190 °C). ^{1}H-NMR (500 MHz, d_6-DMSO, 25 °C): δ_H = 3.90 (s, 3H, NCH_3), 6.83 (d, 2H, ^3J = 7.5 Hz, NPy*H*), 8.06 (brs, 2H, NH_2), 8.14 (d, 2H, ^3J = 7.5 Hz, NPy*H*) ppm. ^{13}C-NMR (125 MHz, d_6-DMSO, 25 °C): δ_C = 44.4, 109.3, 143.8, 158.4 ppm. HR-MALDI-MS (DHB): calcd for $C_6H_9N_2$ ([M–I]$^+$) 109.07603; found 109.07601.

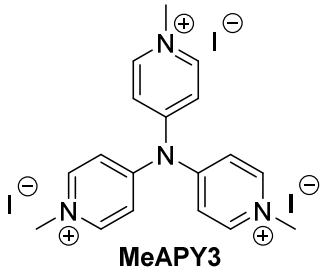
1.5. MeAPY2



MeAPY2

The title compound was prepared from **APY2** (171 mg). White solid. Yield 455 mg (> 99 %). M. p. 170-172 °C. IR (HATR) ν_{max} = 2933, 1623, 1481, 1354, 1194, 1034, 822, 708 cm^{-1}. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 °C): δ_H = 4.25 (s, 6H, NCH_3), 7.85 (d, 4H, ^3J = 7.5 Hz, NPy*H*), 8.80 (d, 2H, ^3J = 7.5 Hz, NPy*H*), 11.62 (brs, 1H, N*H*) ppm. ^{13}C-NMR (125 MHz, d_6-DMSO, 25 °C): δ_C = 46.4, 114.9, 146.1, 151.7 ppm. HR-MALDI-MS (DHB): calcd for $C_{12}H_{14}N_3$ ([M–HI_2]$^+$) 200.11822; found 200.11822.

1.6. MeAPY3



MeAPY3

The title compound was prepared from **APY3** (248 mg). White solid. Yield 671 mg (>99 %). Mp. 145–146 °C. IR (HATR) ν_{max} = 3010, 1633, 1511, 1377, 1194, 855 cm^{-1}. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 °C): δ_H = 4.36 (s, 9H, NCH_3), 8.06 (d, 6H, ^3J = 7.5 Hz, NPy*H*), 9.09 (d, 6H, ^3J = 7.5 Hz, NPy*H*). ^{13}C-NMR (125 MHz, d_6-DMSO, 25 °C): δ_C = 47.1, 122.5, 147.4, 154.6 ppm. HR-MALDI-MS (DHB): calcd for $C_{18}H_{21}N_4$ ([M-3I]$^+$) 293.17607; found 293.17639.

1.7. Synthesis of alpha modification of zirconium hydrogen phosphate

Well-crystallized α modification of $Zr(HPO_4)_2 \cdot H_2O$ (further denoted as **ZrP**), was obtained according to the method proposed by Alberti and Torracca.[4] A clear solution was prepared by dissolving of $ZrOCl_2 \cdot 8H_2O$ (10.1 g), hydrofluoric acid (40% w/w, 8 mL) and H_3PO_4 (85% w/w, 92 mL) in water (160

mL). The solution was heated at 80 °C for 4 days, maintaining a constant volume by continuously adding water. The **ZrP** precipitate was washed with de-ionized water and dried in air.

1.8. Synthesis of a ZrP intercalate with ε-aminocaproic acid

ε-Aminocaproic acid (further denoted as ACA) was intercalated by refluxing ZrP (10 g) in an aqueous solution of ε-aminocaproic acid (0.25 M, 400 mL) for 7 days. The solid product (further denoted as **ZrP·ACA**) was separated by filtration, washed with water and ethanol and dried in air. Its formula was determined to be $Zr(HPO_4)_2 \cdot (H_2N(CH_2)_5COOH)_{0.80} \cdot 1.5H_2O$.[5]

1.9. Synthesis of zirconium 4-sulfophenylphosphonate

Zirconium 4-sulfophenylphosphonate (further denoted as **ZrSPP**) was prepared according to the previously described procedure.[6] 4-Sulfophenylphosphonic acid (2.38 g) and $ZrOCl_2 \cdot 8H_2O$ (2.58 g) were added to a mixture of 1M HF (50 mL) and 1M HCl (50 mL) in a 300-mL PP beaker. The reaction mixture was heated to 80 °C in an oil bath overnight during which time it evaporated to a half of volume. After that, the mixture was evaporated to dryness at 80 °C. The solid was suspended in 1 M HCl and then centrifuged. This process was repeated three times and the obtained slurry was dried in a rotary evaporator at 70 °C to remove hydrochloric acid. The product was dried in a desiccator over NaOH. The sulfophenyl group is partially desulfonated during the synthesis, therefore the formula of the obtained product was determined to be $Zr(HO_3SC_6H_4PO_3)_{1.8}(C_6H_5PO_3)_{0.2} \cdot 2H_2O$.

1.10. Synthesis of gamma modification of titanium hydrogen phosphate

Crystalline γ-titanium phosphate was prepared by hydrothermal treatment of amorphous titanium phosphate.[7] The amorphous titanium phosphate was prepared in a way analogous to that described by Alberti et al.[8] Titanium isopropoxide (0.7 mL) was added to 2.4 M solution of phosphoric acid (10 mL) and the mixture was stirred overnight at room temperature. The amorphous product was separated by centrifugation, placed in a Teflon-lined Parr acid digestion bomb together with phosphoric acid (85%, 9 mL) and the bomb was heated at 220 °C for 48 h. The solid was centrifuged, washed with water and air-dried.

1.11. Synthesis of ZrSPP intercalated with APY1 or APY2

Zirconium 4-sulfophenylphosphonate (0.05 g) and **APY1** (0.06 g) or **APY2** (0.03 g) were added into a mixture of ethanol (5 mL) and water (5 mL) and shaken at room temperature for one week. The obtained products (further denoted as **ZrSPP-APY1** and **ZrSPP-APY2**) were separated from suspension by centrifugation, washed with ethanol and dried in air. Elemental analyses: calcd/found for $Zr(HO_3SC_6H_4PO_3)_{1.8}(C_6H_5PO_3)_{0.2} \cdot 1.2(C_5H_6N_2) \cdot 0.7H_2O$, Mr = 673.04; C, 32.12/31.30 ± 0.01; H,

2.79/2.79 ± 0.01; N, 5.00/5.50 ± 0.01; S, 8.58/8.47 ± 0.02; for $Zr(HO_3SC_6H_4PO_3)_{1.8}(C_6H_5PO_3)_{0.2}\cdot 0.5(C_{10}H_9N_3)\cdot 1.5H_2O$, Mr = 651.11; C, 31.36/30.41 ± 0.01; H, 2.55/2.54 ± 0.01; N, 3.23/3.54 ± 0.01; S, 8.87/8.88 ± 0.01.

1.12. Synthesis of ZrSPP intercalated with APY3

A mixture of zirconium 4-sulfophenylphosphonate (0.05 g) and **APY3** (0.026 g) in water (9 mL) was placed into a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 100 °C for 24 hours. The product (further denoted as **ZrSPP-APY3**) was separated by centrifugation, washed with ethanol and dried in air. Elemental analysis: calcd/found for $Zr(HO_3SC_6H_4PO_3)_{1.8}(C_6H_5PO_3)_{0.2}\cdot 0.35(C_{15}H_{12}N_4)\cdot 1.6H_2O$, Mr = 663.22; C, 31.24/28.93 ± 0.02; H, 2.64/2.59 ± 0.01; N, 2.96/3.12 ± 0.02; S, 8.70/8.32 ± 0.02.

1.13. Synthesis of ZrP intercalated with APY1 or APY2

A mixture of zirconium hydrogen phosphate (0.05 g) and **APY1** (0.060 g) or **APY2** (0.065 g) in water (9 mL) was placed into a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 100 °C for 24 hours. The obtained products (further denoted as **ZrP-APY1** and **ZrP-APY2**) were separated from suspension by centrifugation, washed with ethanol and dried in air. Elemental analyses: calcd/found for $Zr(HPO_4)_2\cdot 0.86(C_5H_6N_2)\cdot H_2O$, Mr = 382.14; C, 13.52/13.63 ± 0.02; H, 2.42/2.48 ± 0.01; N, 6.30/6.29 ± 0.01; for Zr $Zr(HPO_4)_2\cdot 0.43(C_{10}H_9N_3)\cdot 2.25H_2O$, Mr = 397.33; C, 13.00/12.95 ± 0.01; H, 2.63/2.58 ± 0.01; N, 4.55/4.72 ± 0.01.

1.14. Synthesis of ZrP intercalated with APY3

A mixture of **ZrP·ACA** (0.05 g) and **APY3** (0.056 g) in water (9 mL) was placed into a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 100 °C for 24 hours. The obtained products (further denoted as **ZrP-APY3**) were separated from suspension by centrifugation, washed with ethanol and dried in air. Elemental analysis: calcd/found for $Zr(HPO_4)_2\cdot 0.3(C_{15}H_{12}N_4)\cdot 1.75H_2O$, Mr = 389.20; C, 13.89/14.51 ± 0.01; H, 2.36/2.31 ± 0.01; N, 4.32/4.10 ± 0.01.

1.15. Synthesis of TiP intercalated with APY1 or APY2

Titanium hydrogen phosphate (0.05 g) and **APY1** (0.07 g) or **APY2** (0.065 g) were added to a mixture of water (5 mL) and ethanol (5 mL) and the resulting suspension was shaken at room temperature for 4 days. The solid products (further denoted as **TiP-APY1** and **TiP-APY2**) were separated by centrifugation, washed with ethanol and dried in air. Elemental analyses: calcd/found for $Ti(HPO_4)_2\cdot 0.69(C_5H_6N_2)\cdot H_2O$, Mr = 322.79; C, 12.84/12.76 ± 0.02; H, 2.54/2.36 ± 0.02; N, 5.99/6.01 ±

0.01; for $Ti(HPO_4)_2 \cdot 0.35(C_{10}H_9N_3) \cdot 0.75H_2O$, Mr = 313.27; C, 13.42/13.03 ± 0.01; H, 2.14/2.05 ± 0.01; N, 4.69/4.76 ± 0.01.

1.16. Synthesis of TiP intercalated with APY3

A mixture of titanium hydrogen phosphate (0.05 g), **APY3** (0.06 g) and water (9 mL) was placed into a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 100 °C for 24 hours. The product (further denoted as **TiP-APY3**) was separated by centrifugation, washed with ethanol and dried in air. Elemental analysis: calcd/found for $Ti(HPO_4)_2 \cdot 0.22(C_{15}H_{12}N_4) \cdot 2.5H_2O$, Mr = 339.50; C, 11.68/11.86 ± 0.01; H, 2.86/2.80 ± 0.01; N, 3.63/3.40 ± 0.01.

2. Crystallographic data of APY3

The X-ray data for colorless crystals of **APY3** were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[9] The absorption was corrected by integration methods.[10] Structures were solved by direct methods (Sir92)[11] and refined by full matrix least-square based on F^2 (SHELXL97).[12] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = 1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} (methyl). Hydrogen atoms of aromatic rings were placed with C-H distances of 0.93 Å.

$R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1405923 for **APY3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Crystallographic data for **APY3**: $C_{15}H_{12}N_4$, M = 248.29, monoclinic, $P2_1/c$, a = 8.7080(4), b = 15.9311(9), c = 9.5590(6) Å, β = 111.714(4) °, Z = 4, V = 1232.00(12) Å^3, D_c = 1.339 g.cm^{-3}, μ = 0.084 mm^{-1}, T_{min}/T_{max} = 0.979/0.990; $-10 \leq h \leq 11$, $-20 \leq k \leq 19$, $-11 \leq l \leq 12$; 10076 reflections measured (θ_{max} = 27.5 °), 10026 independent (R_{int} = 0.0328), 2267 with $I > 2\sigma(I)$, 172 parameters, S = 1.123, $R1$(obs. data) = 0.0427, $wR2$(all data) = 0.0914; max., min. residual electron density = 0.247, -0.261 eÅ^{-3}.

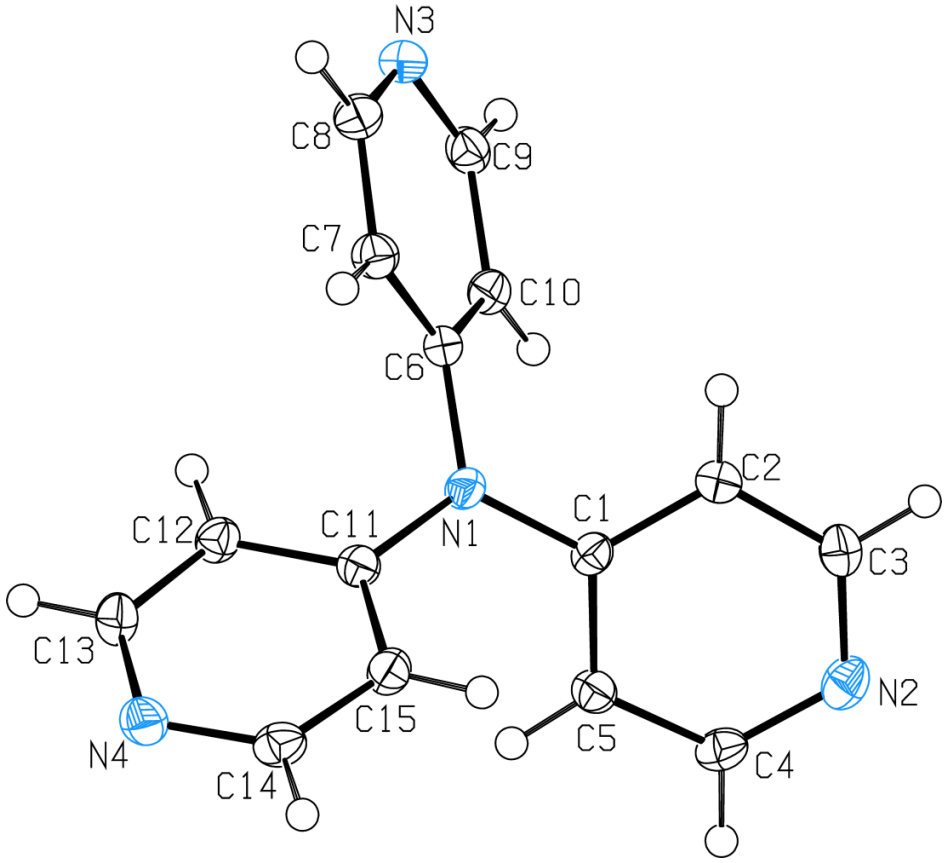
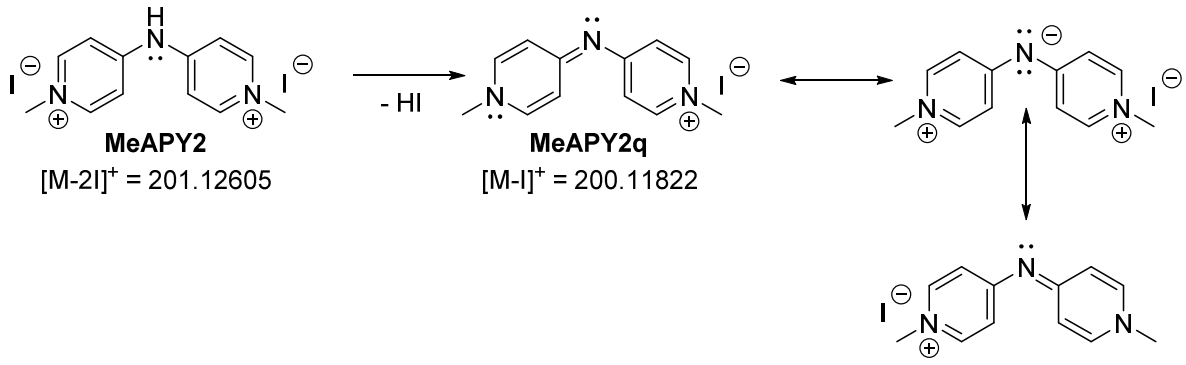


Figure S1. The molecular structure (ORTEP 50% probability level) of **APY3**. Selected interatomic distances [Å] and angles [°]: N2-C3 1.335(2), N2-C4 1.340(2), N3-C8 1.340(2), N3-C9 1.335(2), N4-C13 1.339(2), N4-C14 1.337(2); C3-N2-C4 115.85(13), C9-N3-C8 116.04(13), C14-N4-C13 115.61(13).

3. Structural analysis of MeAPY2

It was observed that pyridinium salt **MeAPY2** undergoes facile loss of HI accompanied by a generation of quinoid structure **MeAPY2q** (Scheme S1). The facile formation of such ion has been detected by HR-MALDI-MS, where this is the only observed peak (Figure S2), and has also significantly affected the UV-Vis spectra (see the main text). Moreover, a significant decrease of pH from 10.46 to 8.56 has been observed after dissolving **MeAPY2** in DMSO (≥99.9% ACS reagent), which further supports liberation of HI in this media.



Scheme S1. Facile loss of HI from **MeAPY2** and concomitant formation of **MeAPY2q**.

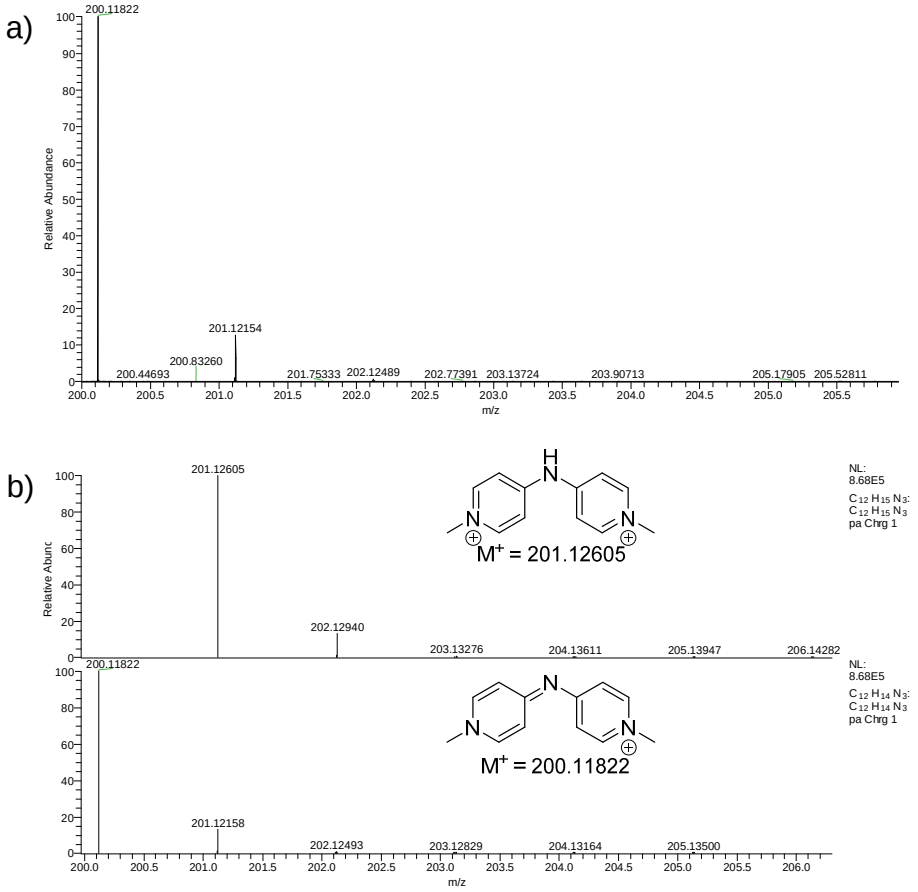


Figure S2. Measured (a) and simulated (b) HR-MALDI-MS spectra of **MeAPY2** and **MeAPY2q** cations.

4. UV-Vis absorption spectra

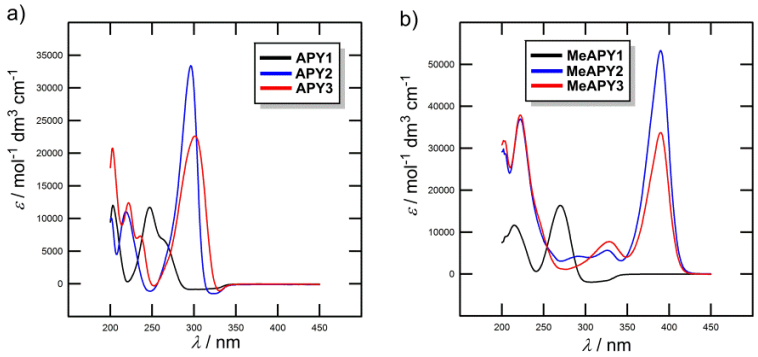


Figure S3. UV-Vis absorption spectra of **APY1-3** (a) and **MeAPY1-3** (b) measured in MeOH ($c = 2\times10^{-5}$ M).

Table S1. Optical data of **APY1-3** and **MeAPY1-3** measured in methanol.

Comp.	λ_{max} (nm(eV))	ε (10^3 M.cm^{-1})
APY1	264(4.70)sh	6.70
APY2	296(4.19)	33.39
APY3	302(4.11)	22.61
MeAPY1	270(4.59)	16.36
MeAPY2	327(3.79)/390(3.18)	5.64/53.29
MeAPY3	329(3.77)/390(3.18)	7.74/33.75

5. DFT calculations

All calculations were carried out in Gaussian 09W (lit.[13]) package at the DFT level of theory. Initial geometry optimizations of molecules **APY1-3** and **MeAPY1-3** were carried out by PM3 method implemented in program ArgusLab (lit.[14]) and subsequently by DFT B3LYP method with 6-311++G(2d,p) basis set. Figure S4 shows the correlation of the calculated (ΔE) and optical gaps ($1240/\lambda_{max}$). The total energies (Table S2) and the Cartesian coordinates are listed below.

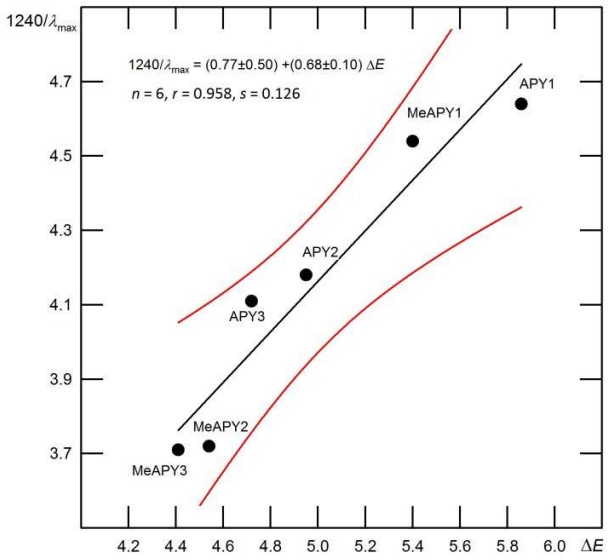


Figure S4. Correlation of the energy of the longest-wavelength absorption maxima $1240/\lambda_{max}$ and the electrochemical gap ΔE.

Table S2. Calculated total energies of **APY1-3** and **MeAPY1-3** (in DMF).

Comp.	E^{total} (10^3 eV)
APY1	-8.265262166
APY2	-14.99043845
APY3	-21.71535256
MeAPY1	-9.347617350
MeAPY2	-17.15462810
MeAPY3	-24.96113521

Cartesian coordinates of **APY1**

N	Atom	X	Y	Z
1	N	-0.53955	0.0000	1.91232
2	C	-0.23129	0.0000	0.64158
3	C	-0.09455	-1.12761	-0.03623
4	C	0.16570	-1.07141	-1.31838
5	N	0.29904	0.0000	-1.97322
6	C	0.16570	1.07141	-1.31838
7	C	-0.09455	1.12761	-0.03623
8	H	-0.34596	0.79614	2.39878
9	H	-0.34596	-0.79614	2.39878
10	H	-0.19298	-2.03434	0.43052
11	H	0.27464	-1.94221	-1.85054
12	H	0.27464	1.94221	-1.85054
13	H	-0.19298	2.03434	0.43052

Cartesian coordinates of **APY2**

N	Atom	X	Y	Z
1	C	-3.43095	0.32499	0.56006
2	N	-3.67171	-0.05200	-0.62079
3	C	-2.67573	-0.41844	-1.30136
4	C	-1.43677	-0.42334	-0.86934
5	C	-1.19250	-0.00932	0.36196
6	C	-2.23415	0.36699	1.08717
7	N	0.0000	0.0000	0.91503
8	C	1.19250	0.00932	0.36196
9	C	1.43677	0.42334	-0.86934
10	C	2.67573	0.41844	-1.30136
11	N	3.67171	0.05200	-0.62079

12	C	3.43095	-0.32499	0.56006
13	C	2.23415	-0.36699	1.08717
14	H	-4.24134	0.61794	1.11695
15	H	-2.87465	-0.74011	-2.25525
16	H	-0.69235	-0.77220	-1.47377
17	H	-2.10766	0.69611	2.04921
18	H	0.0000	0.0000	1.86784
19	H	0.69235	0.77220	-1.47377
20	H	2.87465	0.74011	-2.25525
21	H	4.24134	-0.61794	1.11695
22	H	2.10766	-0.69611	2.04921

Cartesian coordinates of **APY3**

N	Atom	X	Y	Z
1	C	-3.20709	-1.31910	-0.48401
2	N	-3.22144	-2.35562	0.23514
3	C	-2.16647	-2.60925	0.87887
4	C	-1.08522	-1.86756	0.84213
5	C	-1.07876	-0.78800	0.08305
6	C	-2.17658	-0.51549	-0.59684
7	N	0.00023	0.00019	0.00507
8	C	1.22347	-0.54176	-0.03453
9	C	1.46429	-1.63915	-0.72696
10	C	2.68028	-2.13089	-0.73151
11	N	3.65436	-1.61681	-0.11615
12	C	3.41485	-0.56649	0.54046
13	C	2.23481	0.00116	0.61670
14	C	-0.14426	1.33014	-0.03915
15	C	0.61108	2.07543	-0.82382
16	C	0.43047	3.37459	-0.82865

17	N	-0.43343	3.97207	-0.12975
18	C	-1.15252	3.25085	0.61484
19	C	-1.04787	1.94608	0.69964
20	H	-4.06469	-1.12120	-1.01100
21	H	-2.18574	-3.44884	1.46801
22	H	-0.26570	-2.12530	1.39626
23	H	-2.22801	0.30421	-1.20544
24	H	0.72105	-2.10071	-1.25568
25	H	2.88174	-2.98064	-1.26975
26	H	4.20834	-0.15663	1.04519
27	H	2.10662	0.84808	1.17473
28	H	1.32393	1.65320	-1.42262
29	H	1.00771	3.96465	-1.43773
30	H	-1.84823	3.74204	1.18675
31	H	-1.65703	1.42123	1.33095

Cartesian coordinates of **MeAPY1**

N	Atom	X	Y	Z
1	N	-0.16967	0.0000	2.78380
2	C	-0.11257	0.0000	1.52185
3	C	-0.08277	-1.13977	0.82111
4	C	-0.02711	-1.10512	-0.46541
5	N	-0.00120	0.0000	-1.11378
6	C	-0.02711	1.10511	-0.46541
7	C	-0.08277	1.13977	0.82111
8	C	0.10920	0.0000	-2.50434
9	H	-0.19105	0.81264	3.27934
10	H	-0.19106	-0.81264	3.27934
11	H	-0.10696	-2.04633	1.29263
12	H	-0.00246	-1.95824	-1.02645

13	H	-0.00246	1.95824	-1.02645
14	H	-0.10696	2.04633	1.29263
15	H	1.10185	0.0000	-2.77842
16	H	-0.35486	0.83608	-2.87959
17	H	-0.35486	-0.83608	-2.87959

Cartesian coordinates of **MeAPY2**

N	Atom	X	Y	Z
1	C	-3.42237	0.34598	-0.92766
2	N	-3.65311	-0.02090	0.27517
3	C	-2.68428	-0.38573	1.01729
4	C	-1.45577	-0.38533	0.59240
5	C	-1.19137	0.00527	-0.64654
6	C	-2.22039	0.36639	-1.40740
7	N	0.0000	0.0000	-1.18561
8	C	1.19137	-0.00527	-0.64654
9	C	1.45577	0.38533	0.59240
10	C	2.68428	0.38573	1.01729
11	N	3.65311	0.02090	0.27517
12	C	3.42237	-0.34598	-0.92766
13	C	2.22039	-0.36639	-1.40740
14	C	4.96758	0.0000	0.76740
15	C	-4.96758	0.0000	0.76740
16	H	-4.23241	0.62647	-1.48418
17	H	-2.92349	-0.69441	1.96133
18	H	-0.73311	-0.73623	1.22043
19	H	-2.08420	0.67156	-2.37433
20	H	0.0000	0.0000	-2.14225
21	H	0.73311	0.73623	1.22043
22	H	2.92349	0.69441	1.96133

23	H	4.23241	-0.62647	-1.48418
24	H	2.08420	-0.67156	-2.37433
25	H	5.24263	-0.97360	0.95736
26	H	5.59424	0.41538	0.06663
27	H	5.00916	0.55001	1.63298
28	H	-5.59424	-0.41538	0.06663
29	H	-5.00916	-0.55001	1.63298
30	H	-5.24263	0.97360	0.95736

Cartesian coordinates of **MeAPY3**

N	Atom	X	Y	Z
1	N	0.0000	0.00015	-0.00802
2	C	-0.98638	0.91198	0.00979
3	C	-0.29663	-1.30983	-0.03333
4	C	1.28300	0.39833	-0.00224
5	N	-2.91010	2.69673	0.03993
6	N	-0.88064	-3.86775	-0.08749
7	N	3.79071	1.17184	0.00420
8	C	-2.06932	0.76147	-0.73545
9	C	0.38638	-2.15032	-0.79350
10	C	2.19014	-0.23227	0.72529
11	C	-1.28310	-1.80058	0.69874
12	C	1.68072	1.43193	-0.72633
13	C	-0.90487	1.99091	0.77082
14	C	0.07407	-3.41500	-0.80103
15	C	-1.55022	-3.07502	0.65291
16	C	-3.00831	1.66376	-0.70096
17	C	-1.87559	2.86000	0.76664
18	C	3.42791	0.17431	0.71010
19	C	2.93207	1.79339	-0.70432

20	C	-1.17149	-5.24719	-0.09193
21	C	-3.95913	3.63766	0.08058
22	C	5.13065	1.60911	0.03288
23	H	1.03707	1.94793	-1.32937
24	H	-1.83713	-1.21110	1.32304
25	H	1.94731	-1.02481	1.32288
26	H	-0.10620	2.15887	1.38573
27	H	1.14411	-1.83394	-1.40174
28	H	-2.18521	-0.03574	-1.36411
29	H	0.56772	-4.09027	-1.38903
30	H	-2.29360	-3.49186	1.21759
31	H	-3.85040	1.58992	-1.27615
32	H	-1.85464	3.69618	1.35451
33	H	4.15203	-0.27779	1.27267
34	H	3.27882	2.57543	-1.26433
35	H	-0.59470	-5.71156	0.62381
36	H	-3.57050	4.56065	0.30765
37	H	-2.16843	-5.37839	0.11635
38	H	-0.95876	-5.62897	-1.02155
39	H	-4.41280	3.66999	-0.84047
40	H	5.23356	2.31932	0.77154
41	H	5.73958	0.80529	0.22673
42	H	-4.63669	3.35026	0.80095
43	H	5.36888	2.01140	-0.88178

6. Thermogravimetric analysis of intercalates

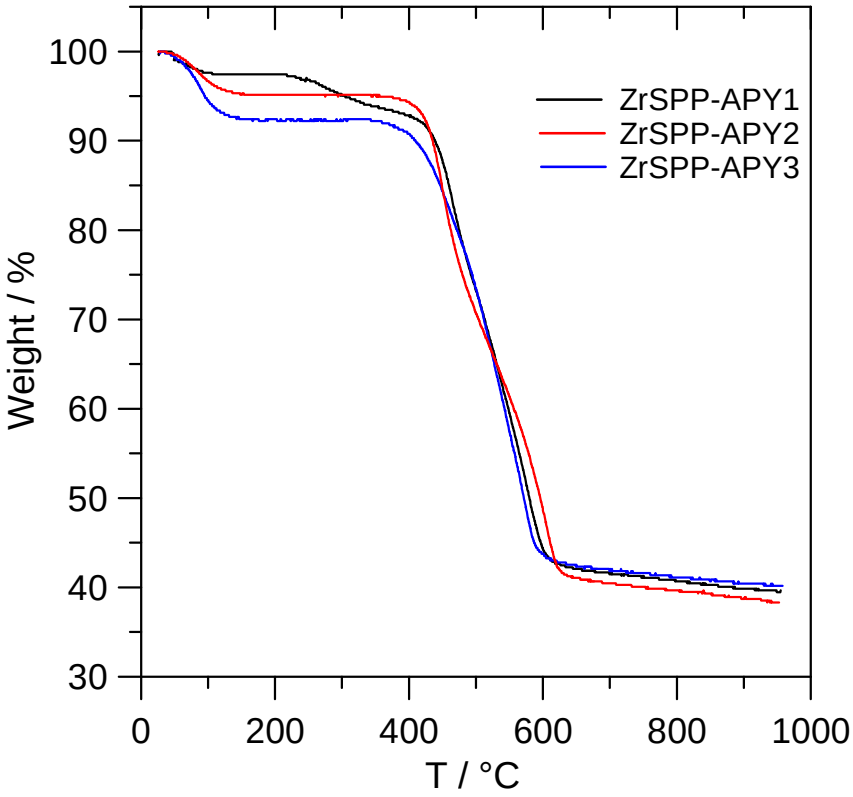


Figure S5. Thermogravimetric curves for the intercalates of **ZrSPP** with **APY1-3**.

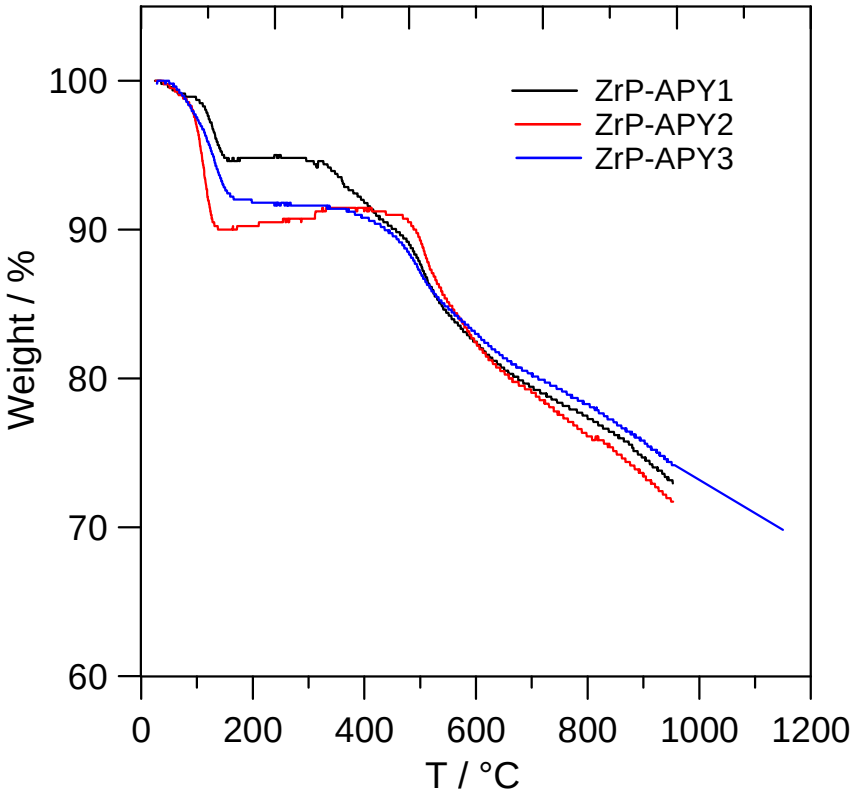


Figure S6. Thermogravimetric curves for the intercalates of **ZrP** with **APY1-3**.

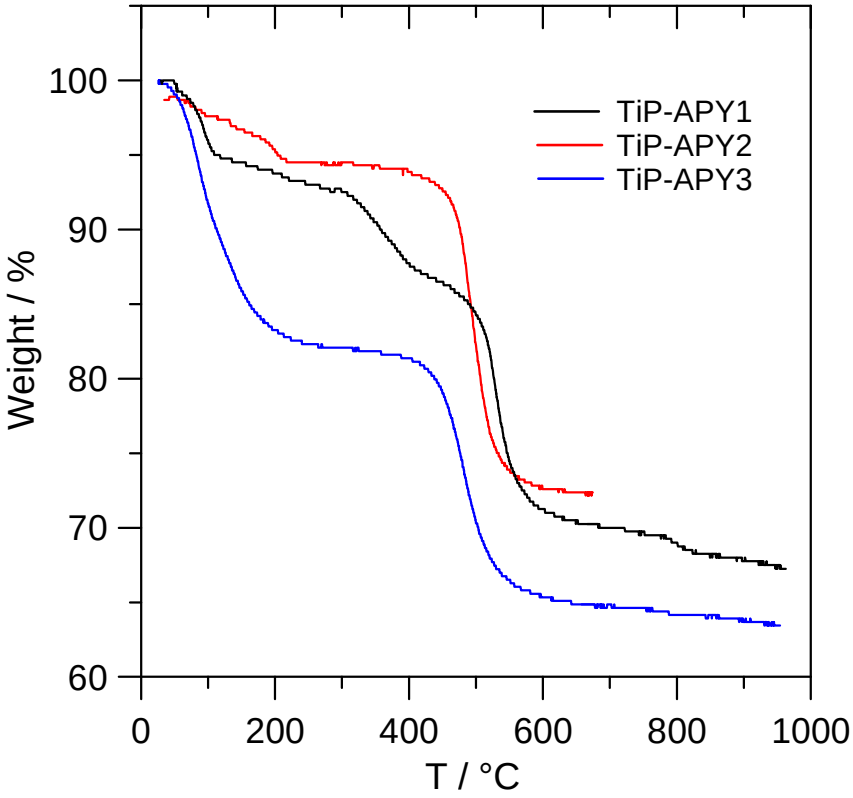


Figure S7. Thermogravimetric curves for the intercalates of **TiP** with **APY1-3**.

7. Infrared spectra

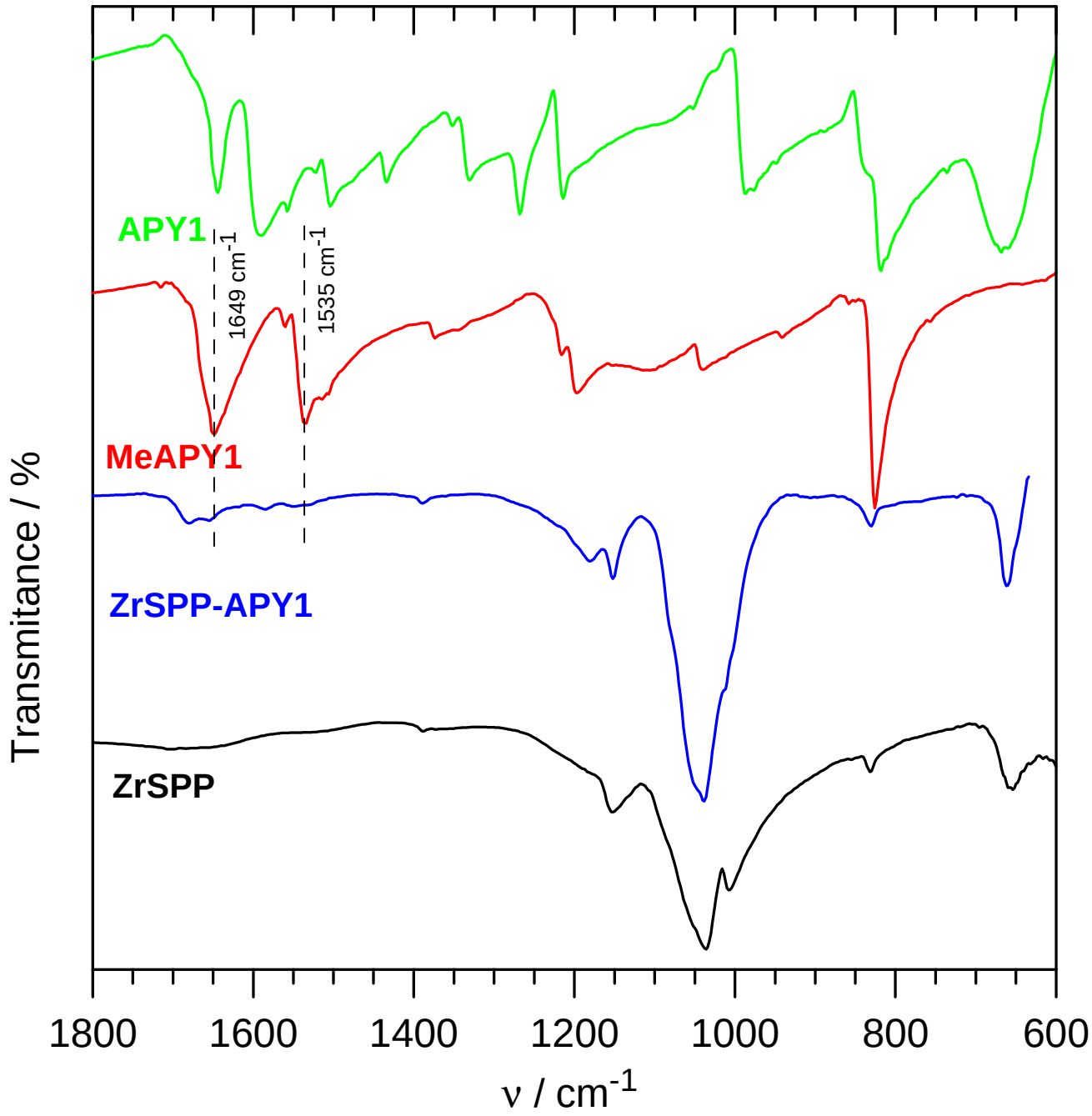


Figure S8. The IR spectrum of **ZrSPP** intercalated with **APY1** (**ZrSPP-APY1**) and its comparison with the IR spectra of the pristine host (**ZrSPP**), pure **APY1** and its methylated analogue **MeAPY1**.

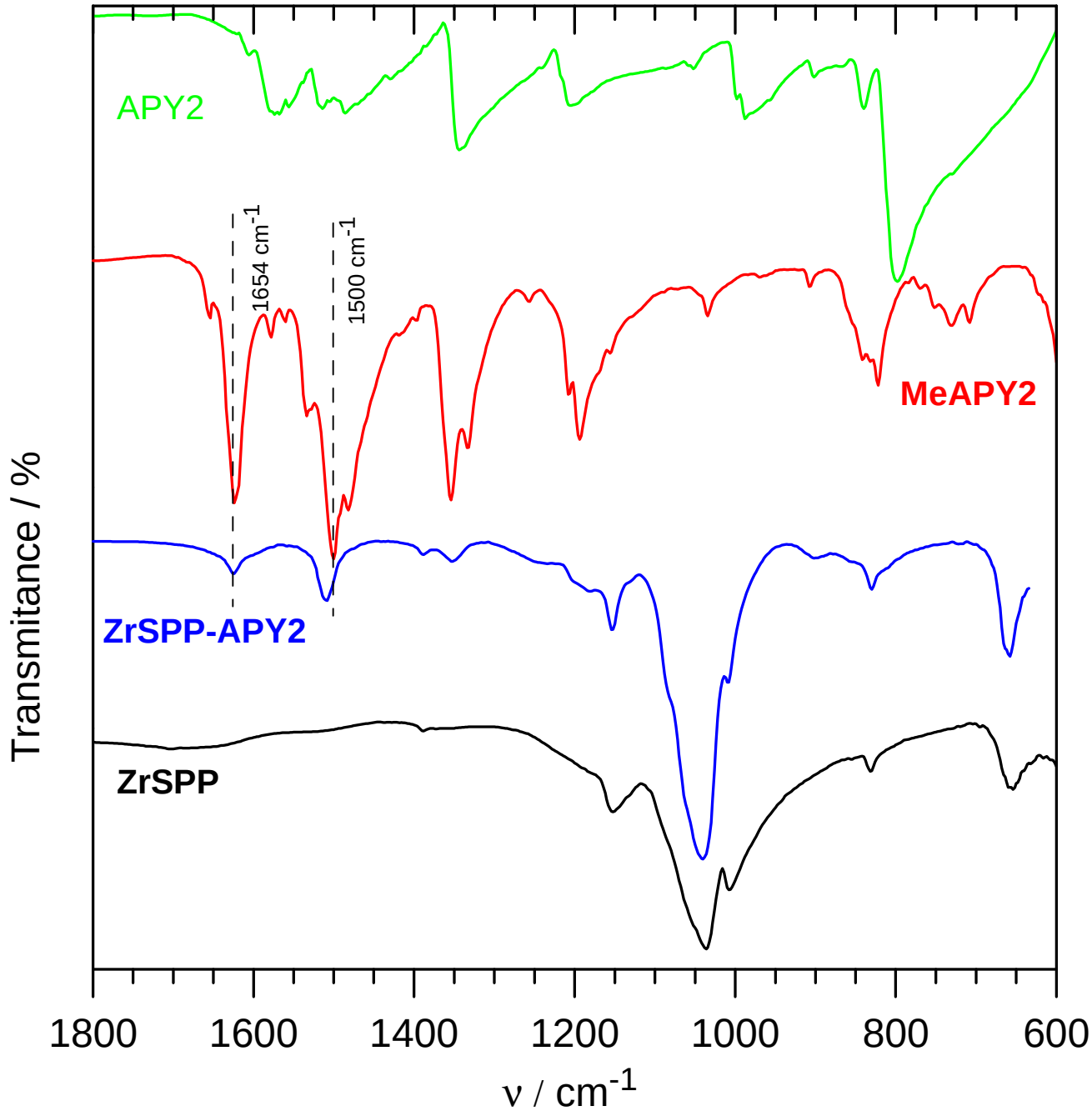


Figure S9. The IR spectrum of **ZrSPP** intercalated with **APY2** (**ZrSPP-APY2**) and its comparison with the IR spectra of the pristine host (**ZrSPP**), pure **APY2** and its methylated analogue **MeAPY2**.

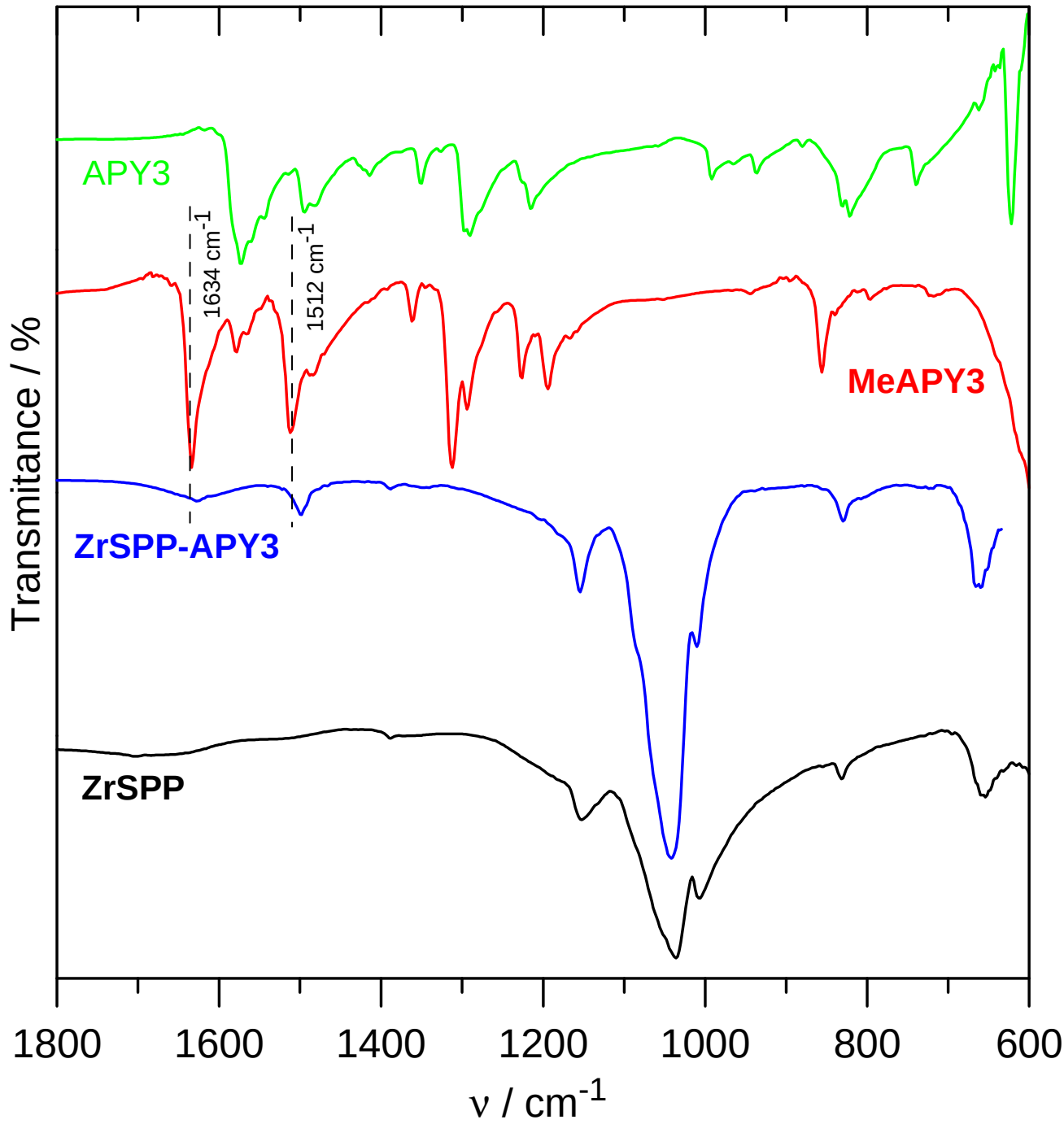


Figure S10. The IR spectrum of **ZrSPP** intercalated with **APY3** (**ZrSPP-APY3**) and its comparison with the IR spectra of the pristine host (**ZrSPP**), pure **APY3** and its methylated analogue **MeAPY3**.

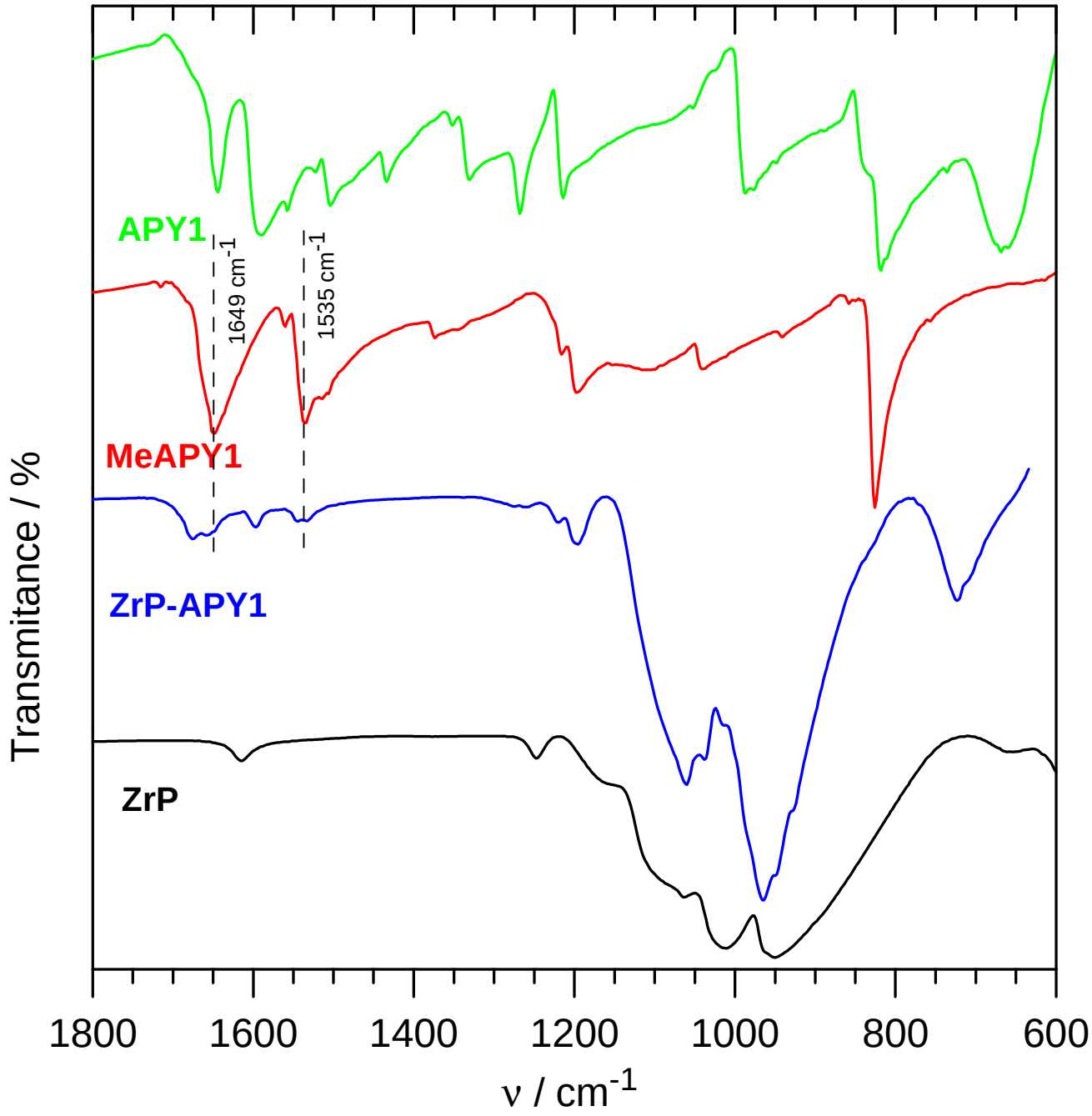


Figure S11. The IR spectrum of **ZrP** intercalated with **APY1** (**ZrP-APY1**) and its comparison with the IR spectra of the pristine host (**ZrP**), pure **APY1** and its methylated analogue **MeAPY1**.

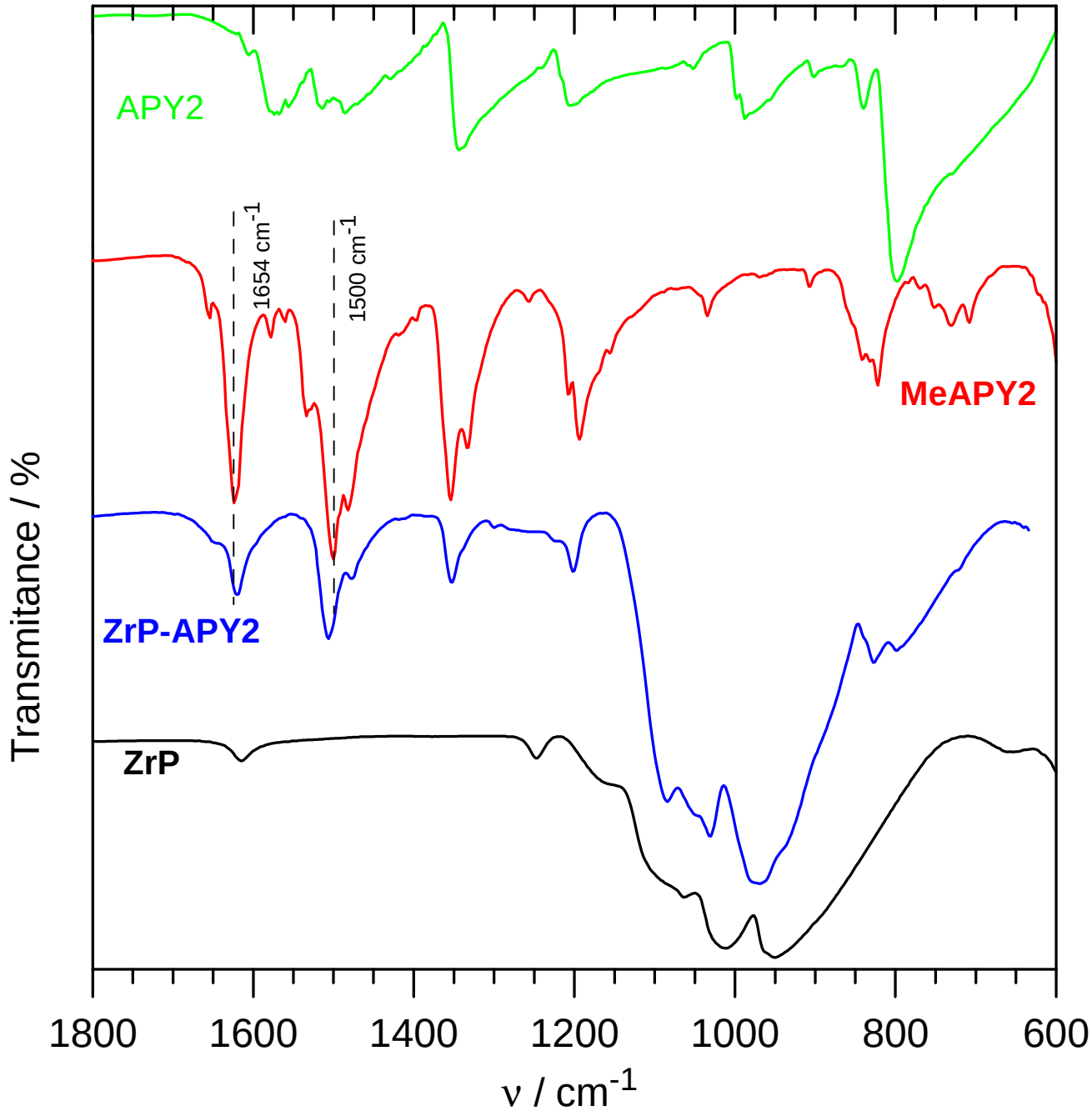


Figure S12. The IR spectrum of **ZrP** intercalated with **APY2** (**ZrP-APY2**) and its comparison with the IR spectra of the pristine host (**ZrP**), pure **APY2** and its methylated analogue **MeAPY2**.

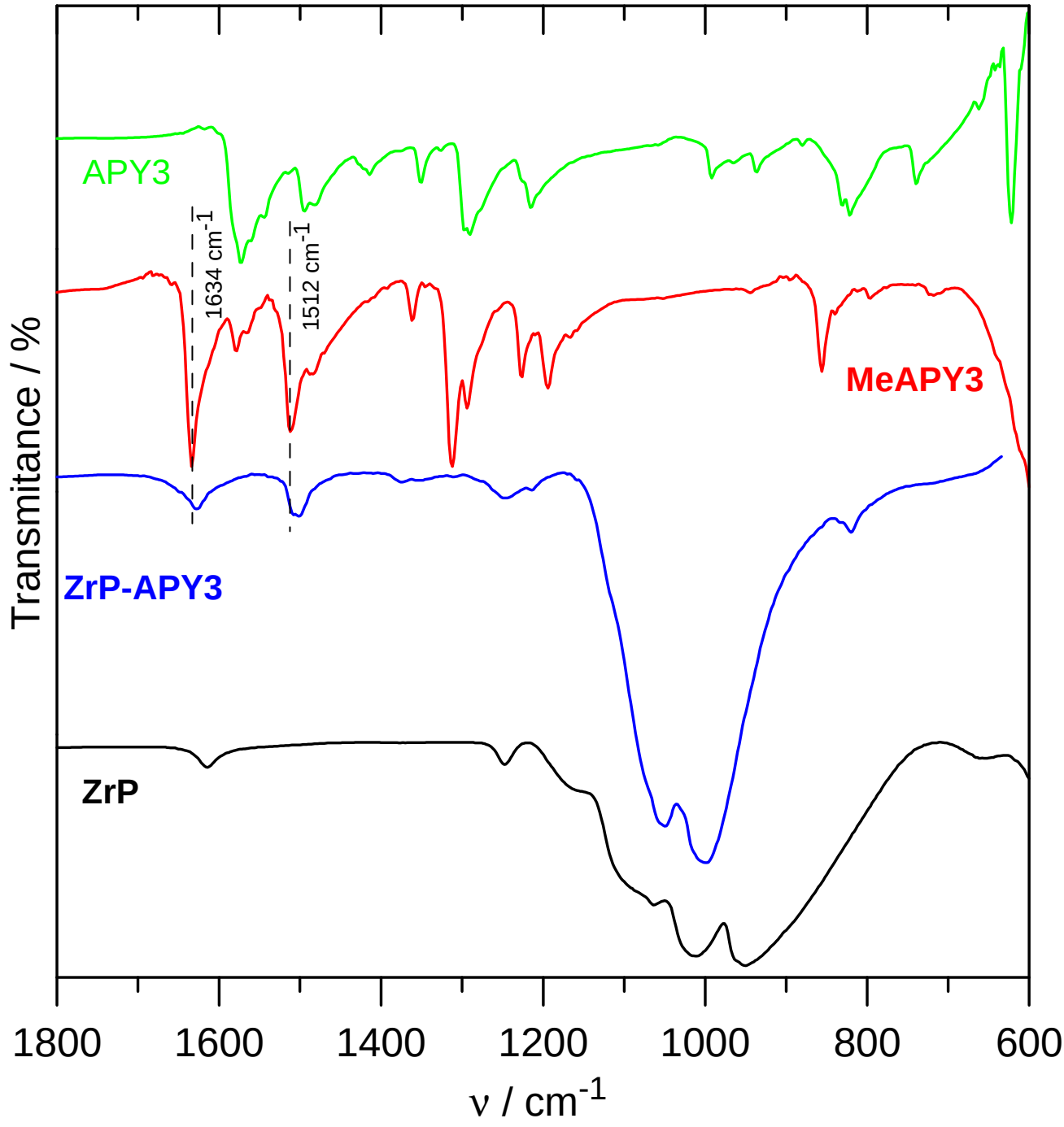


Figure S13. The IR spectrum of **ZrP** intercalated with **APY3** (**ZrP-APY3**) and its comparison with the IR spectra of the pristine host (**ZrP**), pure **APY3** and its methylated analogue **MeAPY3**.

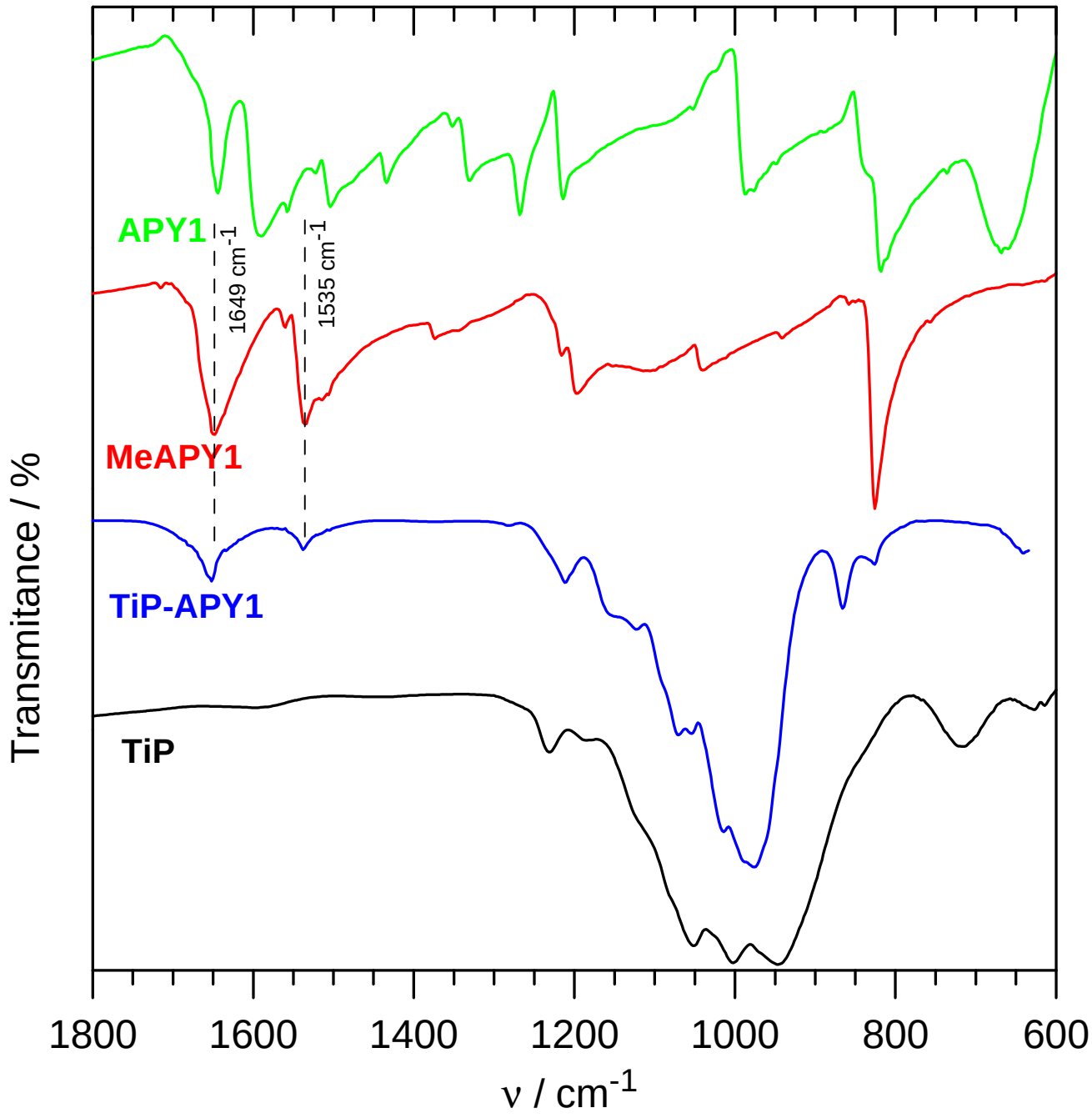


Figure S14. The IR spectrum of **TiP** intercalated with **APY1** (**TiP-APY1**) and its comparison with the IR spectra of the pristine host (**TiP**), pure **APY1** and its methylated analogue **MeAPY1**.

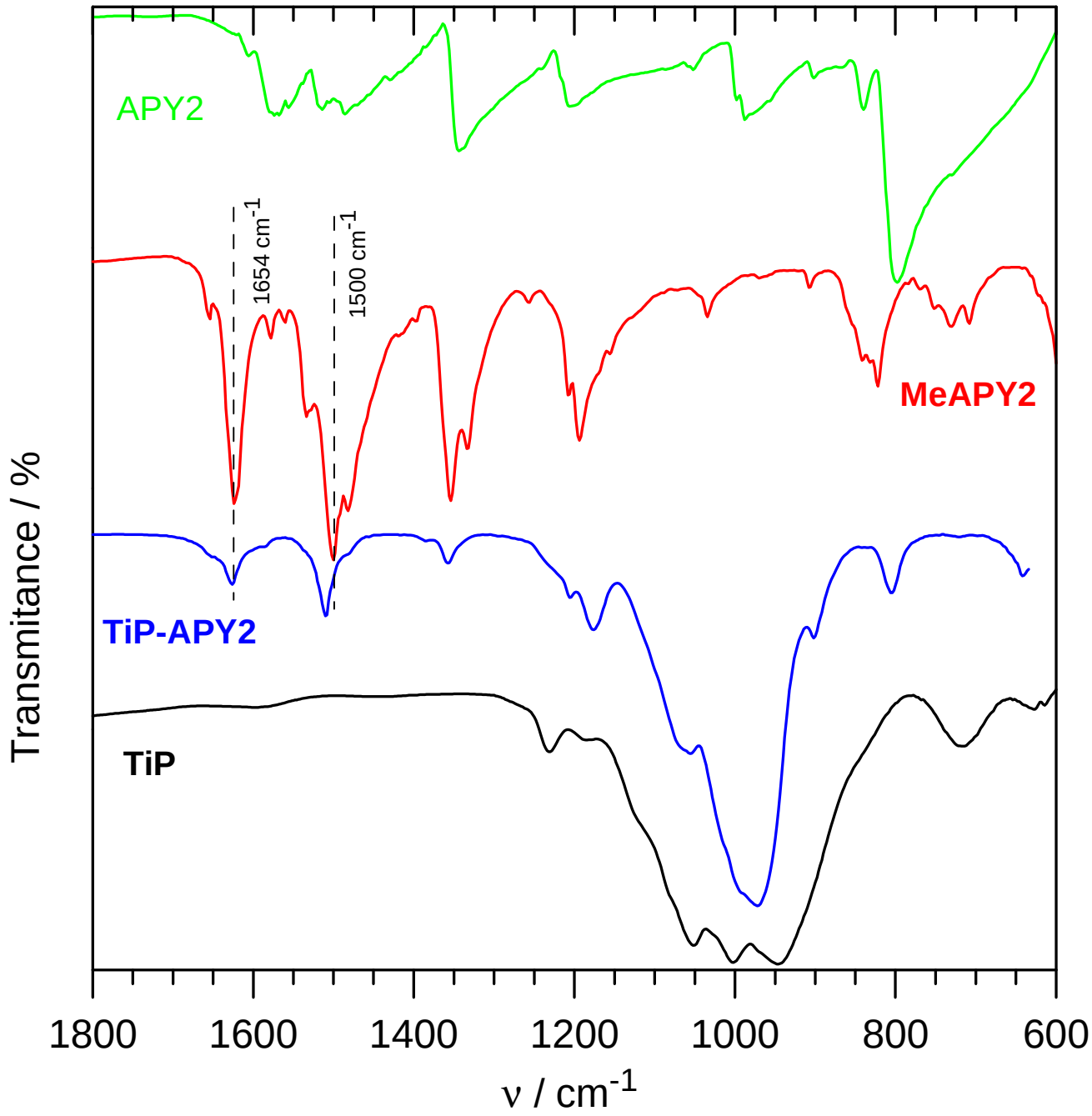


Figure S15. The IR spectrum of **TiP** intercalated with **APY2** (**TiP-APY2**) and its comparison with the IR spectra of the pristine host (**TiP**), pure **APY2** and its methylated analogue **MeAPY2**.

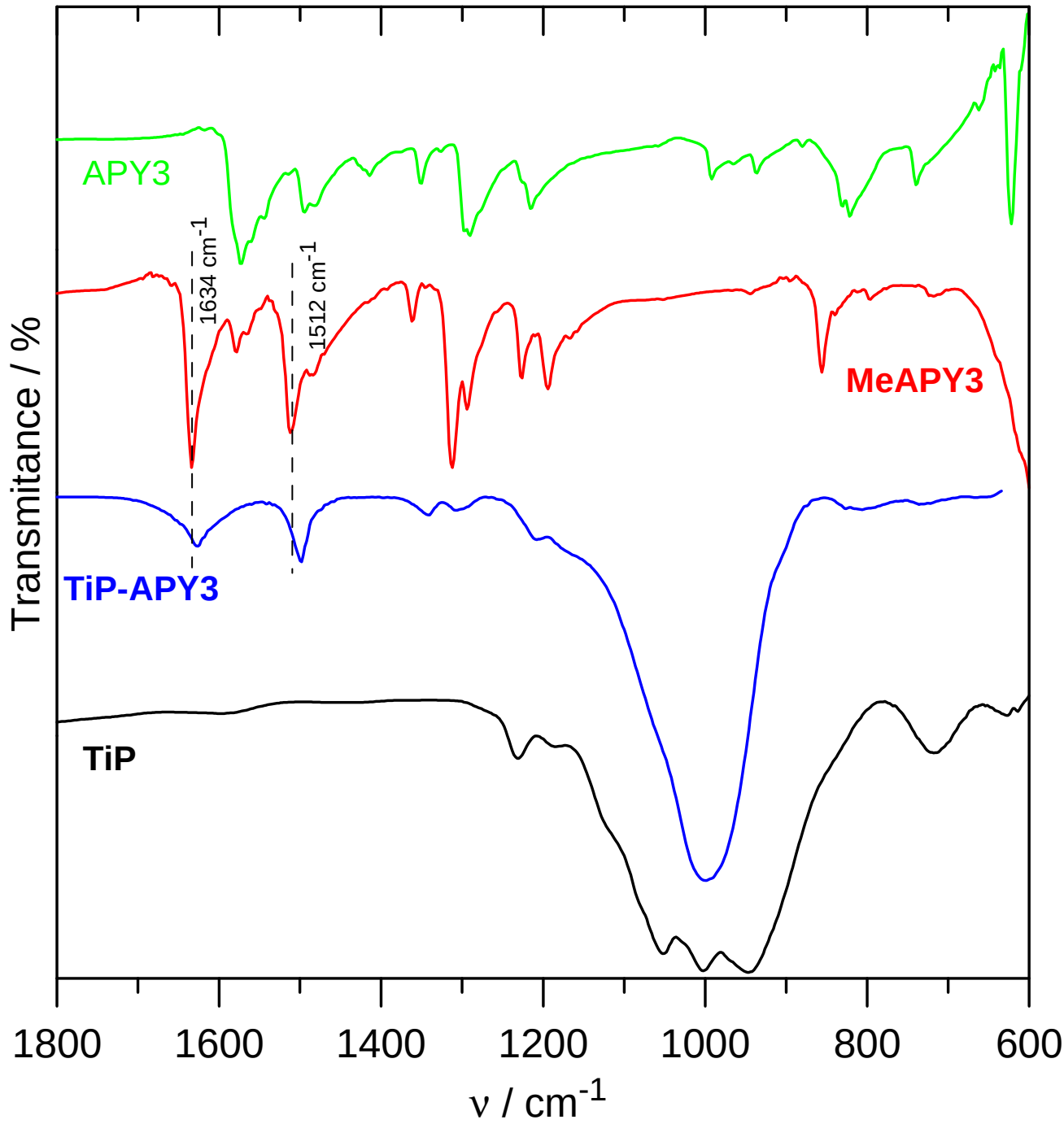


Figure S16. The IR spectrum of **TiP** intercalated with **APY3** (**TiP-APY3**) and its comparison with the IR spectra of the pristine host (**TiP**), pure **APY3** and its methylated analogue **MeAPY3**.

8. Solid-state UV/Vis spectra

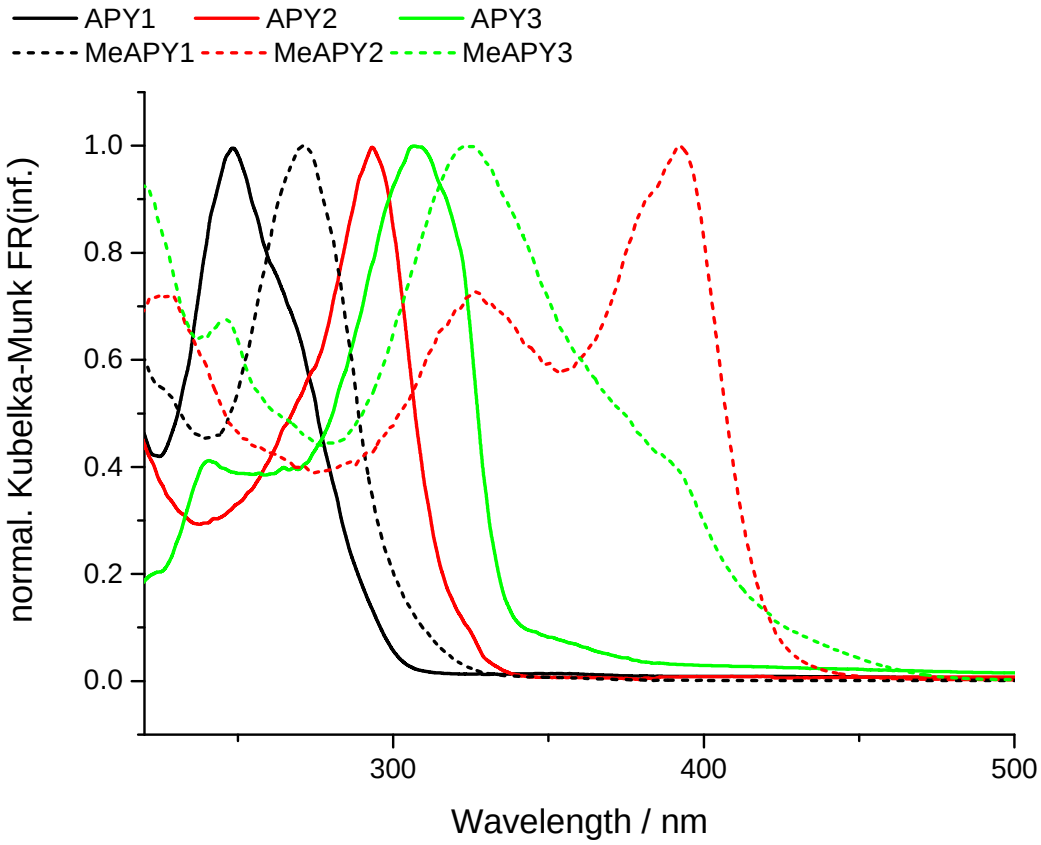


Figure S17. The solid-state UV/Vis spectra of **APY1-3** and their methylated analogues **MeAPY1-3**.

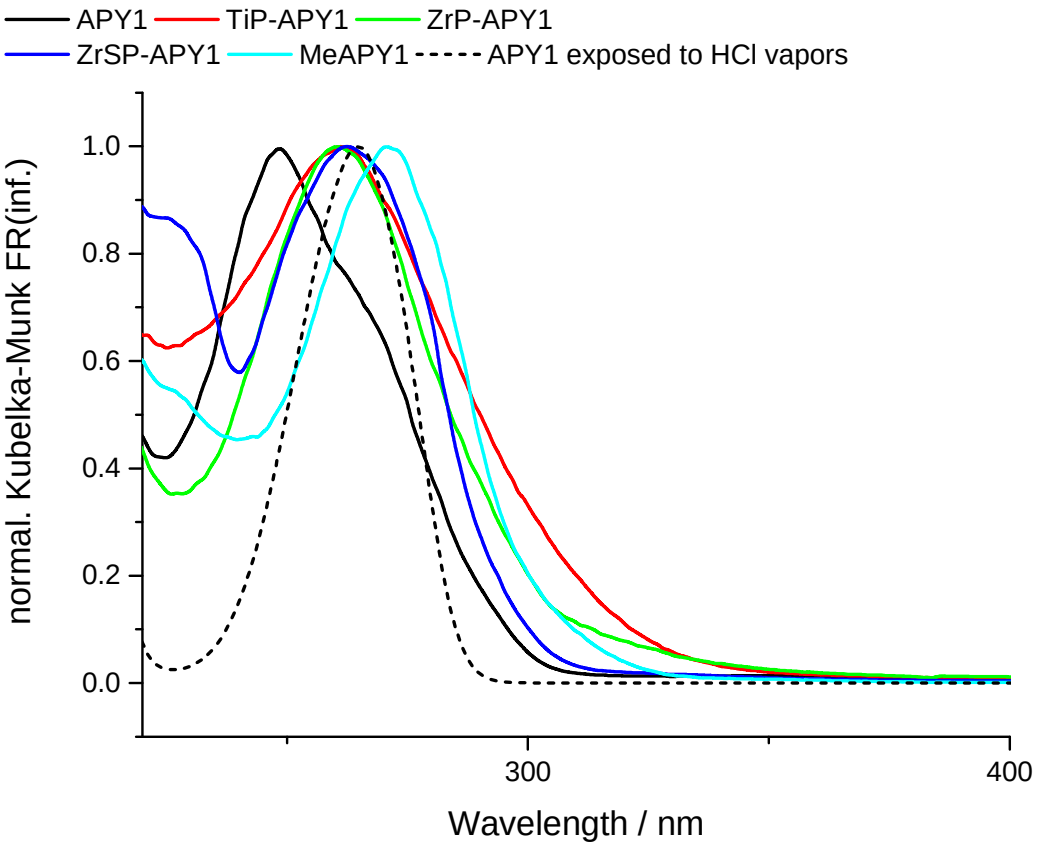


Figure S18. The solid-state UV/Vis spectra of the intercalates of **APY1**.

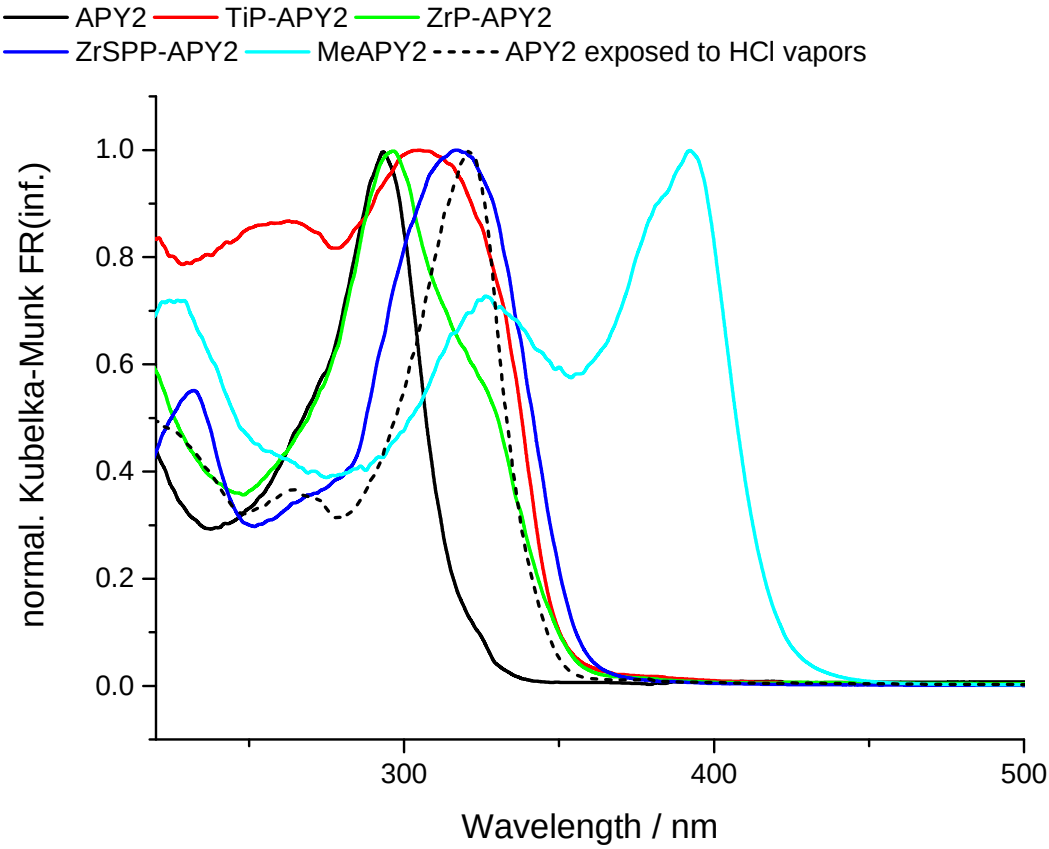


Figure S19. The solid-state UV/Vis spectra of the intercalates of **APY2**.

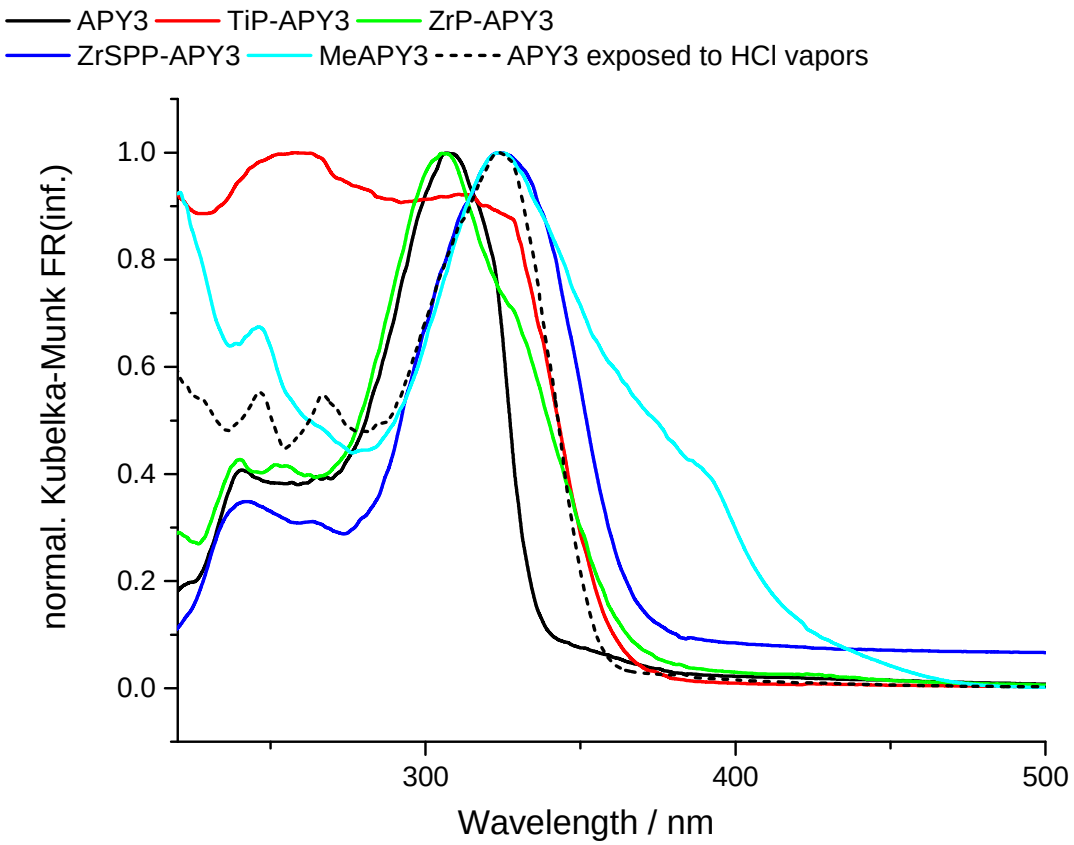


Figure S20. The solid-state UV/Vis spectra of the intercalates of **APY3.**

Table S3. Optical data of **APY1-3**, their intercalates, and **MeAPY1-3** measured in the solid-state.

Guest	Host	λ_{max} (nm(eV))
APY1	-	248(5.00)
APY1	**ZrSPP**	263(4.71)
APY1	**ZrP**	260(4.77)
APY1	**TiP**	261(4.75)
APY1	in HCl	265(4.68)
MeAPY1	-	271(4.58)
APY2	-	293(4.23)
APY2	**ZrSPP**	317(3.91)
APY2	**ZrP**	297(4.18)
APY2	**TiP**	305(4.07)
APY2	in HCl	321(3.86)
MeAPY2	-	326(3.80)/392(3.16)
APY3	-	307(4.04)
APY3	**ZrSPP**	323(3.84)
APY3	**ZrP**	305(4.06)
APY3	**TiP**	315(3.94)
APY3	in HCl	324(3.83)
MeAPY3	-	323(3.84)/392(3.16)

9. NLO measurements

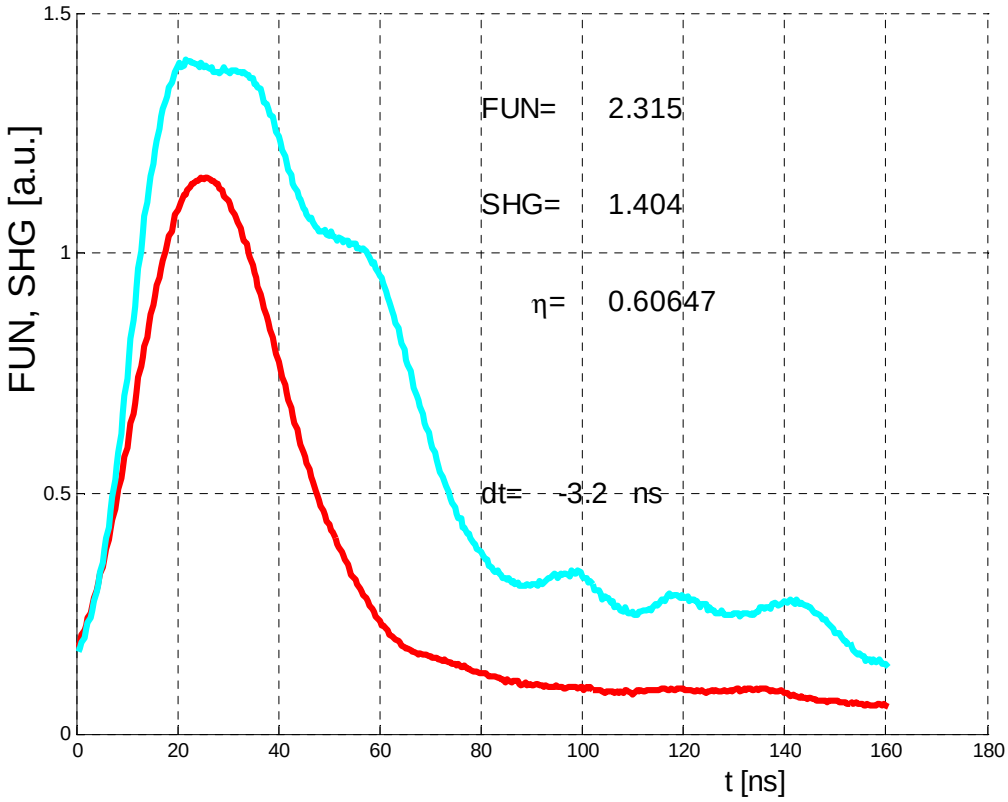


Figure S21. Representative dependence of the time kinetics of the fundamental (red) and the SHG films. The scale is renormalized for the different scales of **APY2** for better imaging. One can see some time shift of the corresponding maxima. For other chromophore, the dependences are similar.

Table S4. Calculation of the free volumes in the intercalates

	V_{APY} (Å^3)	V_{guest} (Å^3)			d_g (Å)			V_H (Å^3)			V_H - V_{guest} (Å^3)		
		ZrSPP	**ZrP**	**TiP**	**ZrSPP**	**ZrP**	**TiP**	**ZrSPP**	**ZrP**	**TiP**	**ZrSPP**	**ZrP**	**TiP**
APY1	94	112	80	64	7.48	6.35	6.50	179	152	107	66	150	42
APY2	165	82	71	58	7.11	7.12	5.96	170	170	98	87	168	40
APY3	236	82	70	52	9.59	6.50	6.28	233	155	103	150	153	52

V_{APY} - calculated volume of the **APY** molecule based on the van der Waals surface obtained after geometry optimization using MM+ method, molecular mechanics force field, embedded in a Hyperchem software[15]

V_{guest} - volume of the guest molecule in the intercalate per formula unit calculated as $V_{guest} = V_{APY} \times x$, where x is the amount of the intercalated guest given in Table 2

d_g - gallery height calculated as $d_g = d - d_l$, *where* d is the basal spacing taken from Table 3 and d_l is the host layer thickness (16.8, 6.3 and 9.2 Å for **ZrSPP**, **ZrP**, and **TiP**, respectively)

V_H - volume accessible for the intercalated guest molecules in the intercalates per formula unit, calculated as $V_H = d_g \times A_F/2$, where A_F is free area per formula unit of the corresponding host (48 Å^2 for **ZrSPP** and **ZrP** and 32.9 Å^2 for **TiP**)

10. References

1. E. Koenigs, G. Jung, *J. Pract. Chem.*, 1933, **137**, 141.

2. R. S. Alekseev, A. V. Kurkin, M. A. Yurovskaya, *Chem. Heterocycl. Compd.*, 2012, **48**, 1235.

3. W. R. Abrams, R. G. Kallen *J. Am. Chem. Soc.*, 1976, **98**, 7777.

4. G. Alberti, E. Torraca, *J. Inorg. Nucl. Chem.*, 1968, **30**, 317.

5. Y. Ding, D. J. Jones, P. Maireles-Torres, J. Roziere, *Chem. Mater.*, 1995, **7**, 562.

6. V. Zima, J. Svoboda, K. Melánová, L. Beneš, M. Casciola, M. Sganappa, J. Brus, M. Trchová, *Solid State Ionics*, 2010, **181**, 705.

7. A. M. K. Andersen, P. Norby, *Inorg. Chem.*, 1998, **37**, 4313.

8. G. Alberti, P. Cardini-Galli, U. Costantino, E. Torraca, *J. Inorg. Nucl. Chem.*, 1967, **29**, 571.

9. Z. Otwinowski, W. Minor, *Methods in Enzymology* (Processing of X-ray diffraction data collected in oscillation mode), 1997, **276**, 307.

10. P. Coppens, In: F. R. Ahmed, S. R. Hall, C. P. Huber, Eds., *Crystallographic Computing*, 1970, pp. 255-270, Copenhagen, Munksgaard.

11. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.*, 1994, **27**, 1045.

12. G. M. Sheldrick, SHELXL-97, University of Göttingen: Göttingen, **2008**.

13. Gaussian 09, Revision D.01, Frisch, M.J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

14. ArgusLab, Mark Thompson and Planaria Software LLC, Version 4.01, webpage: http://www.arguslab.com.

15. Hyperchem, Release 5. Standalone version; Computational Chemistry, Hypercube Inc.: Gainesville, USA, 1996.