Crystal engineering with 1,3,5-triaza-7-phosphaadamantane (PTA): first PTA-driven 3D metal-organic frameworks

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Electronic Supplementary Information (ESI)

ESI contains materials and methods, synthesis and full characterization of **1** and **2**, refinement details for the single-crystal X-ray analyses, luminescent properties, supplementary references and Figures S1−S7.

1. Materials and methods

All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, except 1,3,5-triaza-7-phosphaadamantane (PTA) that was prepared by a published method.[S1] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX or a Bruker IFS 1113v instruments in KBr pellets (abbreviations: vs− very strong, s − strong, m – medium, w – weak, br. – broad, sh. – shoulder). ESI-MS(±) spectra were run on a 500-MS LC Ion Trap instrument (Varian Inc, Alto Palo, CA, USA) equipped with an electrospray (ESI) ion source, using ca. 10^{-3} M solutions of **1** and **2** in H_2O/MeOH. ^1H and $^{31}P\{^1H\}$ NMR spectra were measured on a Bruker 300 AMX spectrometer at ambient temperature. The ^{31}P chemical shifts are relative to an external 85% H_3PO_4 aqueous solution. Photoluminescence spectra were measured with a SpectraPro 750 monochromator equipped with Hamamatsu R928 photomultiplier and 1200 l/mm grating blazed at 500 nm. The 450 W xenon arc lamp was used as an excitation source, coupled with 275 mm excitation monochromator using a 1800 l/mm grating blazed at 250 nm. Excitation spectra were corrected for the excitation light intensity, while emission spectra were corrected for the instrument response. The concentration of the samples in aqueous solution was 5×10^{-4} M. Emission kinetic was measured with a Tektronix TDS 3052B oscilloscope and Nd:YAG Lambda Physics pulsed laser (λ_{exc}=355 nm).

2. Synthesis and characterization of 1 and 2

$[Ag_2(\mu_2\text{-bpca})(\mu_3\text{-PTA})_2]_n\cdot 2nH_2O$ (1). Silver(I) oxide (0.1 mmol, 23 mg) and H_2dpca (0.15 mmol, 36 mg) were combined in a solution containing CH_2Cl_2/MeOH/H_2O (5 mL / 5 mL / 0.5 mL), which was left stirring for 30 min at room temperature (r.t., ca. 20 ºC). Then PTA (0.2 mmol, 31 mg) was added and the reaction mixture was stirred further for 30 min to produce a white precipitate, which was almost completely dissolved by a dropwise addition of an aqueous 1M solution of NH_4OH (ca. 0.5 mL, until pH ≈ 8.5). The obtained cloudy solution was filtered off, and the filtrate was left in a vial to evaporate slowly in air at r.t. Colourless crystals (including those of X-ray quality) were formed in 1-2 weeks, then collected and dried in air to give **1** in ~50% yield, based on Ag_2O. $S_{25\,°C}$ (in H_2O) ≈ 1.0 mg mL^{-1}. Found for **1**: C, 39.14; H, 4.06; N, 10.37. $C_{26}H_{36}Ag_2N_6O_6P_2$ (806.3) requires C, 38.73; H, 4.50; N, 10.42. IR

(KBr)/cm^{-1}: 3403 (w br.) and 3224 (w br.) ν(H_2O), 2940 (w) ν_{as}(CH), 2859 (w) ν_s(CH), 1645 (w) δ(H_2O), 1586 (vs) and 1541 (s) ν_{as}(COO), 1480 (m) and 1386 (s) ν_s(COO), 1439 (w), 1286 (s), 1235 (s), 1142 (vs), 1093 (w), 1011 (m), 951 (vs), 934 (s), 837 (s), 807 (m), 764 (m), 677 (s), 585 (s), 563 (m) and 460 (m). ESI-MS(±) (H_2O/MeOH), selected fragments with relative abundance >10%: MS(+), *m/z*: 771 (25%) $[Ag_2(PTA)_2(Hbpca)]^+$, 421 (100%) $[Ag(PTA)_2]^+$, 264 (70%) $[Ag(PTA)]^+$; MS(−), *m/z*: 803 (10%) $[Ag_2(PTA)_2(bpca)(H_2O)_2 - H]^-$, 589 (15%) $[Ag(Hbpca)_2]^-$, 504 (20%) $[Ag(PTA)(bpca)]^-$, 365 (10%) $[Ag(bpca)(H_2O)]^-$, 241 (100%) $[Hbpca]^-$. ^{1}H NMR (300 MHz, D_2O, Me_4Si): δ 7.94 (d, 4H, $H_{3,3',5,5'}$, $^3J_{3\text{-}2} = {}^3J_{5\text{-}6} = {}^3J_{3'\text{-}2'} = {}^3J_{5'\text{-}6'}$ = 8.4 Hz, bpca), 7.77 (d, 4H, $H_{2,2',6,6'}$, bpca), 4.57 and 4.48 (2d, 12H, J_{AB} = 13.0 Hz, NCH^AH^BN, PTA), 4.19 (d, 12H, $^3J_{P\text{-}H}$ = 1.5 Hz, PCH_2N, PTA). ^{31}P{^{1}H} NMR (121.4 MHz, D_2O, 85% H_3PO_4): δ −79.5 (s, PTA).

$[Ag_4(\mu_4\text{-pma})(\mu_2\text{-PTA})_2(\mu_3\text{-PTA})_2]_n \cdot 8nH_2O$ (2). Compound **2** was prepared by following the procedure described for **1** but by using H_4pma (0.25 mmol, 64 mg) instead of H_2dpca and a different amount of NH_4OH (ca. 1.0 mL). Colourless crystals (including those of X-ray quality) were obtained in ~50% yield, based on Ag_2O. $S_{25\ °C}$ (in H_2O) ≈ 0.6 mg mL^{-1}. Found for **2**: C, 28.14; H, 4.59; N, 11.59. $C_{34}H_{66}Ag_4N_{12}O_{16}P_4$ (1454.3) requires C, 28.08; H, 4.57; N, 11.56. IR (KBr)/cm^{-1}: 3410 (vs br.) ν(H_2O), 2925 (w) and 2895 (w) ν_{as}(CH), 2850 (w) ν_s(CH), 1645 (m sh.) δ(H_2O), 1571 (vs br.) and 1484 (w) ν_{as}(COO), 1414 (s) and 1375 (s) ν_s(COO), 1324 (w), 1293 (m), 1240 (s), 1136 (w), 1097 (m), 1035 (w), 1014 (s), 974 (s), 961 (m), 947 (s), 897 (m), 863 (w), 807 (m), 791 (m), 749 (m), 720 (w), 596 (m), 582 (m), 520 (w), 457 (m) and 436 (w). ESI-MS(+) (H_2O/MeOH), selected fragments with relative abundance >20%: *m/z*: 1449 (30%) $[Ag_5(PTA)_4(pma)(H_2O)_2 + Ag]^+$, 1312 (20%) $[Ag_4(PTA)_4(Hpma)]^+$, 781 (30%) $[Ag_2(PTA)_2(H_3pma)]^+$, 679 (90%) $[Ag_4(Hpma)]^+$, 573 (60%) $[Ag_3(H_2pma)]^+$, 421 (100%) $[Ag(PTA)_2]^+$, 264 (30%) $[Ag(PTA)]^+$. ^{1}H NMR (300 MHz, D_2O, Me_4Si): δ 7.53 (s, 2H, $H_{3,6}$, pma), 4.63 and 4.52 (2d, 24H, J_{AB} = 13.0 Hz, NCH^AH^BN, PTA), 4.25 (d, 24H, $^3J_{P\text{-}H}$ = 2.0 Hz, PCH_2N, PTA). ^{31}P{^{1}H} NMR (121.4 MHz, D_2O, 85% H_3PO_4): δ −78.2 (s, PTA).

3. Refinement details for the single-crystal X-ray analyses

The X-ray diffraction data of **1** and **2** were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5º per frame, and a full sphere of data was obtained. Cell parameters

were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS.[S2] Structures were solved by direct methods using SIR97[S3] program and refined with SHELXL–97.[S4] Calculations were performed with the WinGX System-Version 1.80.03.[S5] All hydrogen atoms were inserted in calculated positions. In **2**, heavily disordered crystallization water molecules in the large accessible voids could not be modeled satisfactorily and thus were handled with PLATON/SQUEEZE.[S6] Diamond and TOPOS software packages were used for structural visualization.[S7]

4. Supplementary references

S1. (a) D. J. Daigle, A. B. Pepperman Jr. and S. L. Vail, *J. Heterocycl. Chem.*, 1974, **11**, 407. (b) D. J. Daigle, *Inorg. Synth.*, 1998, **32**, 40.

S2. Bruker, *APEX2 & SAINT*; AXS Inc.: Madison, WI, 2004.

S3. A. Altomare, M. C. Burla, M. C. Camalli, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

S4. G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

S5. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

S6. A. L. Spek, *Acta Crystallogr.*, 1990, **C46**, C34.

S7. (a) K. Brandenburg, *Diamond.* Crystal Impact GbR, Bonn, Germany, 2006. (*b*) V. A. Blatov, *IUCr CompComm Newsletter*, **2006**, *7*, 4.

5. Supplementary figures

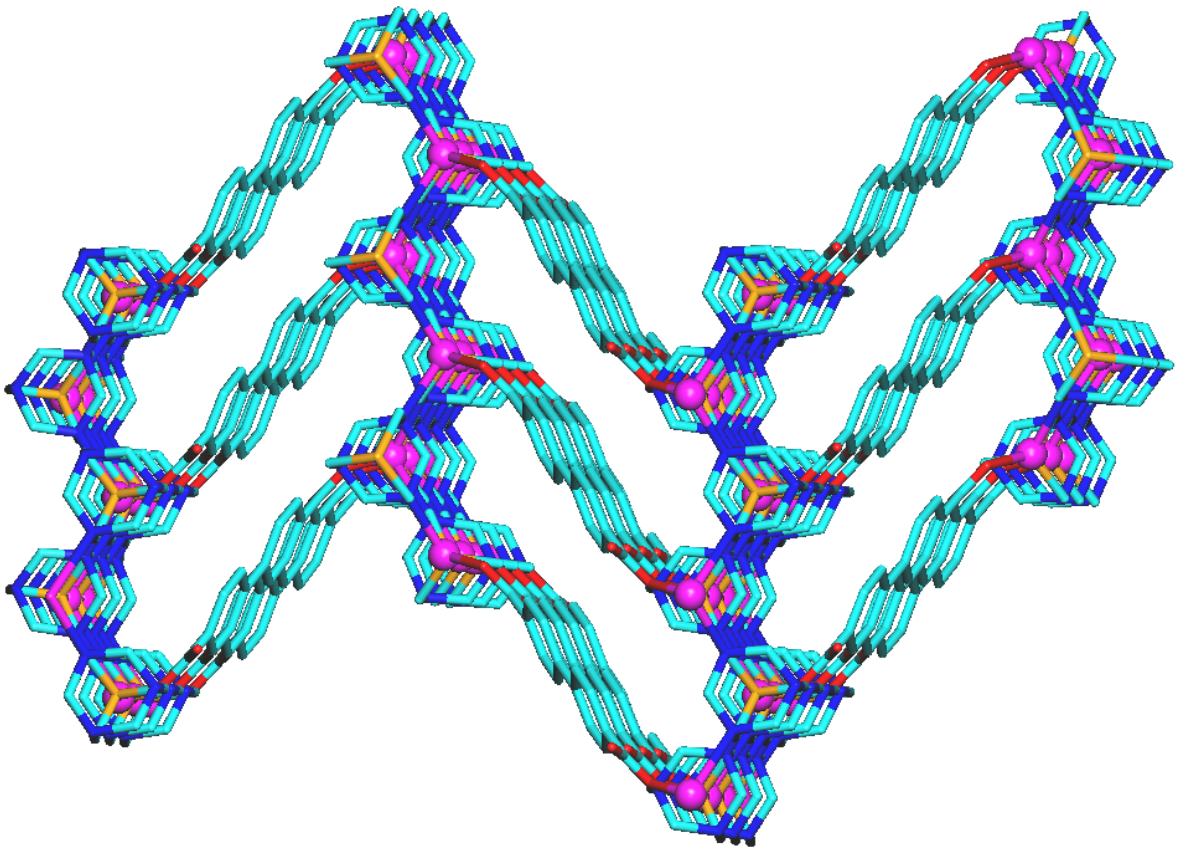

Fig. S1 Layer-pillared wave-like 3D framework of **1** (rotated view along the *c* axis). H atoms and crystallization H_2O molecu1es are omitted for clarity, colour codes: Ag balls (magenta), N (blue), P (orange), O (red), C (cyan).

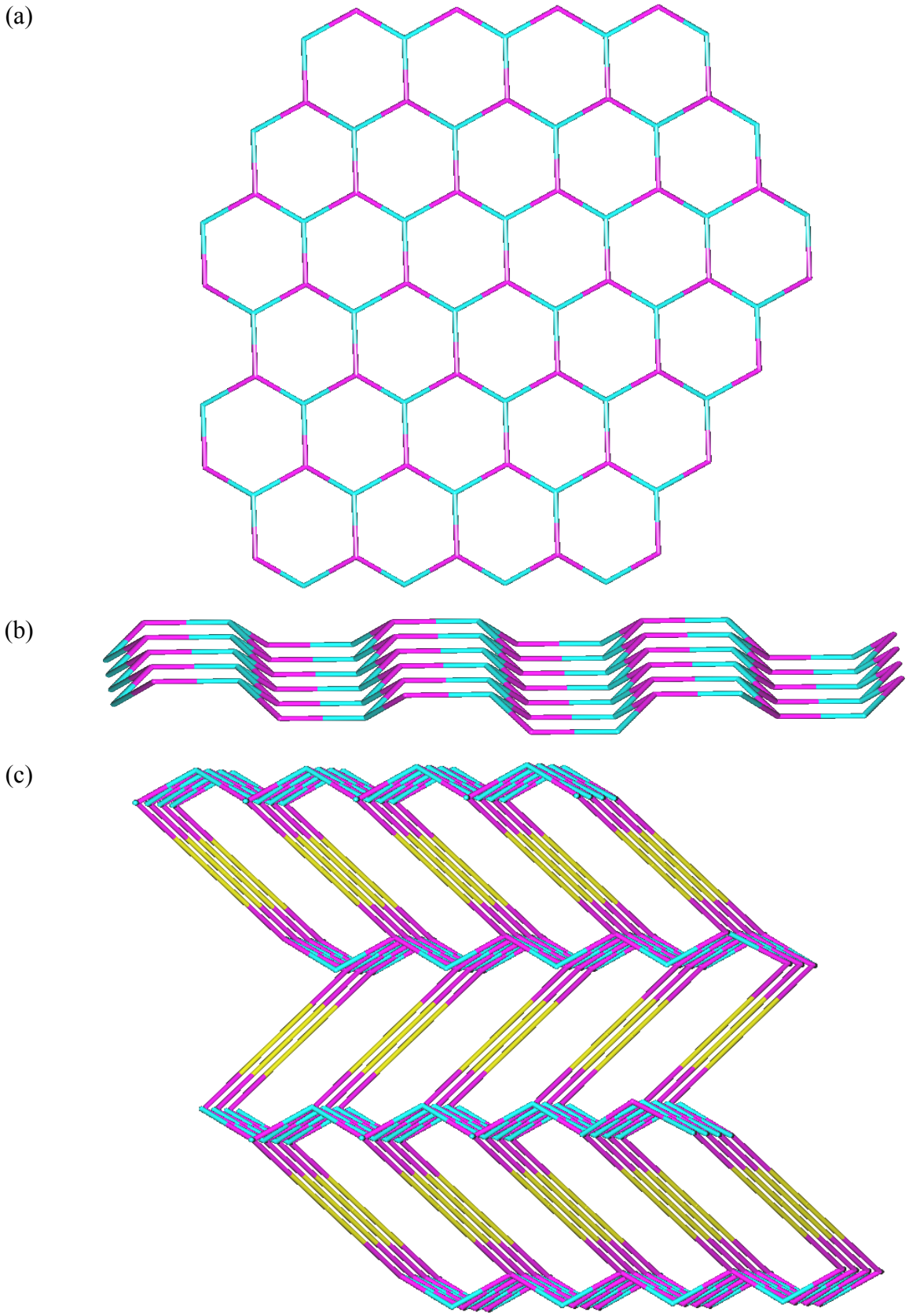

Fig. S2 Topological representations of **1**: (a)−(b) one hexagonal (honeycomb-like) PTA-driven 2D layer [rotated views along the *b* (a) and *a* (b) axes]; (c) simplified underlying 3,4-connected **ins** net that features a herringbone-like pattern if viewed along the *c* axis. Colour codes: centroids of 3-connected μ_3-PTA nodes (cyan), 4-connected Ag1 nodes (magenta), centroids of μ_2-bpca linkers (yellow).

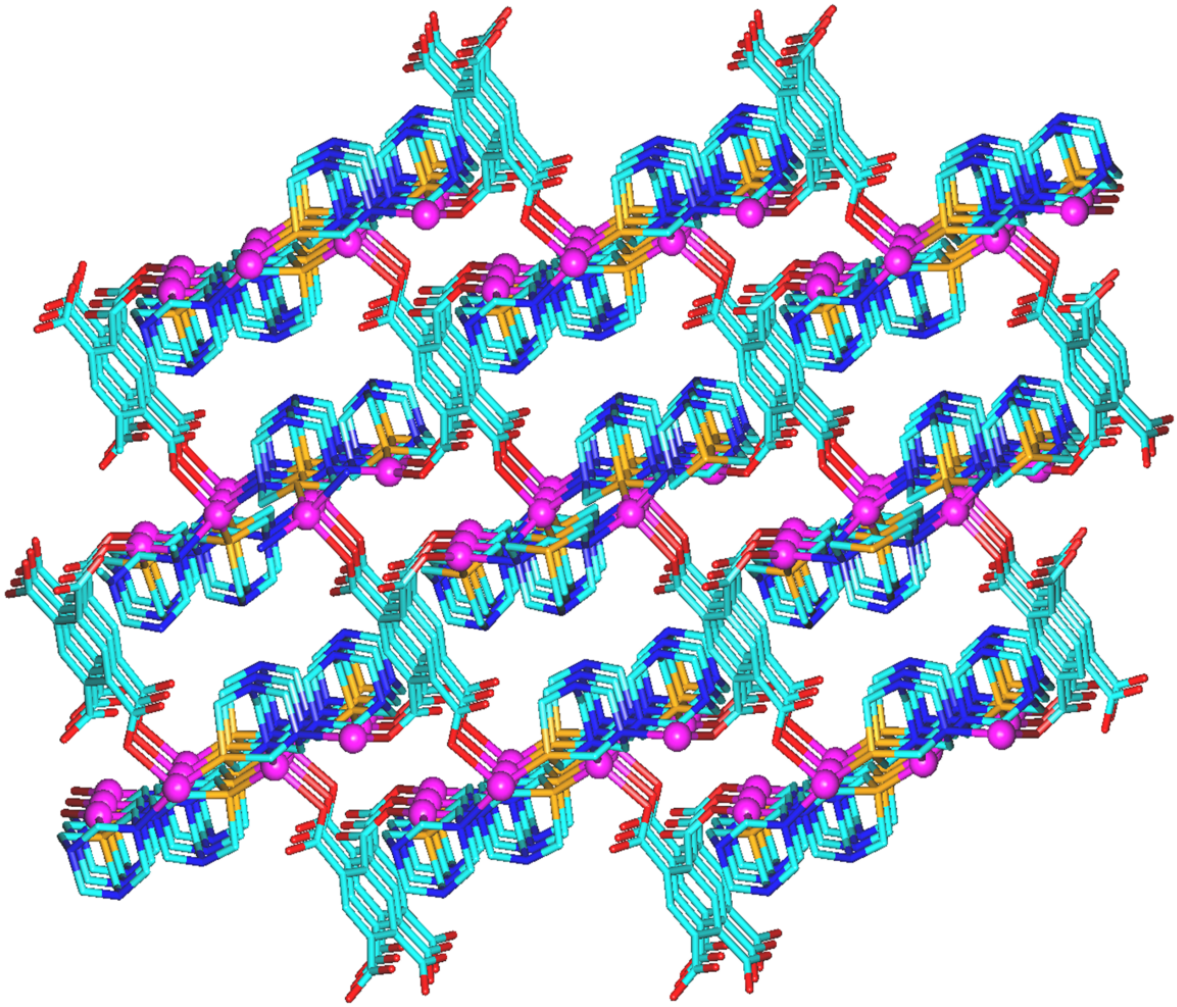

Fig. S3 Complex 3D framework of **2** assembled from PTA-driven 1D ribbons and μ_4-pma pillars (rotated view along the *b* axis). H atoms are omitted for clarity, colour codes: Ag balls (magenta), N (blue), P (orange), O (red), C (cyan).

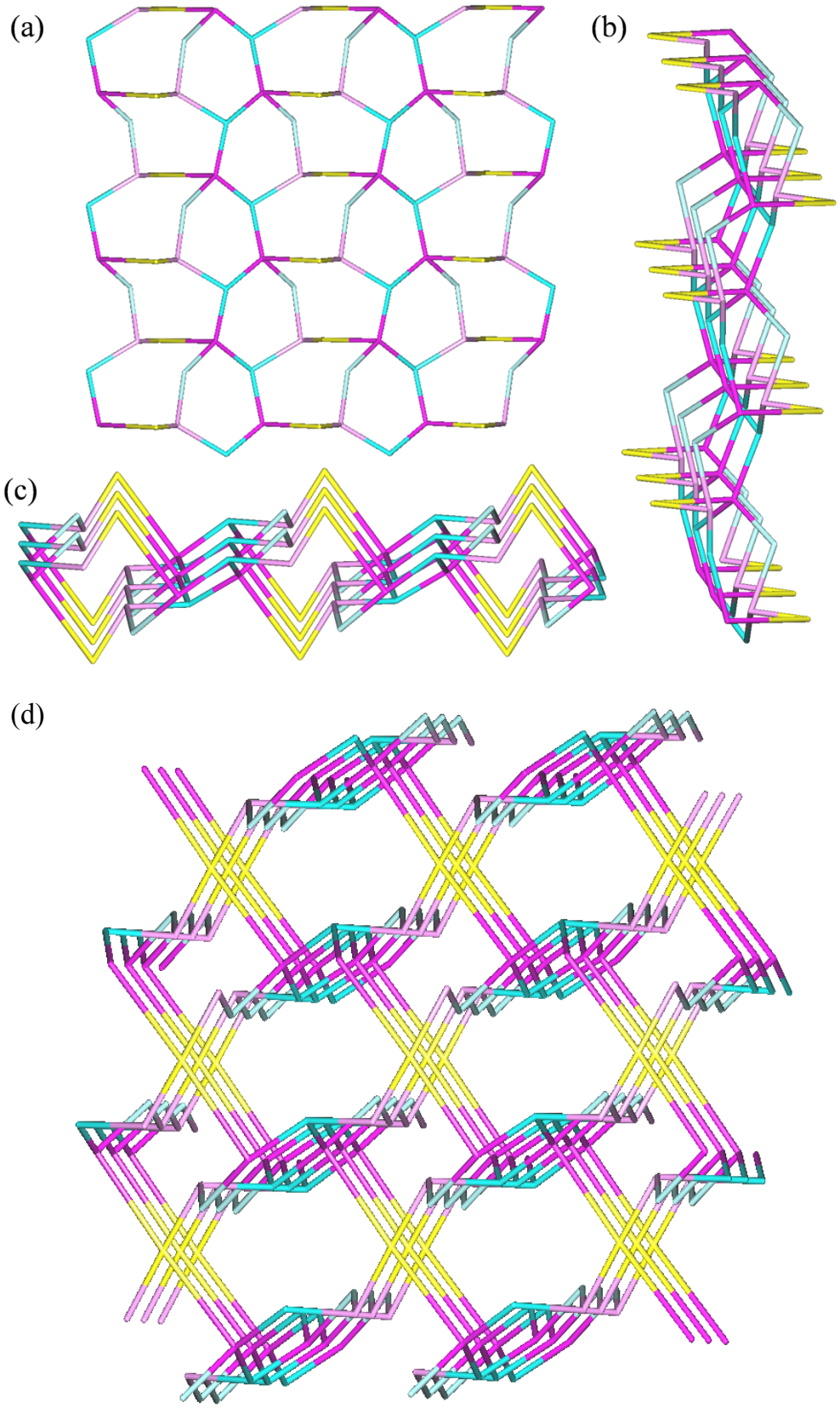

Fig. S4 Topological representations of **2**: front (a) and side (b, c) views of one lace-like 2D layer constructed through the junction of adjacent PTA-driven 1D ribbons [rotated views along the *c* (a), *a* (b) and *b* (c) axes, only a half of the pma nodes is shown]; (d) simplified underlying 3,3,4,4-connected tetranodal net with the point symbol of $(5.7^2)_2(5^2.7^2.8^2)_2(5^2.7)_2(7^2.8^2.10^2)$ [rotated view along the *b* axis]. Colour codes: centroids of 3-connected μ_3-PTA nodes (cyan), 3-connected Ag3 and Ag4 nodes (pale pink), 4-connected Ag1 and Ag2 nodes (magenta), centroids of 4-connected μ_4-pma nodes (yellow), and centroids of μ_2-PTA linkers (pale blue).

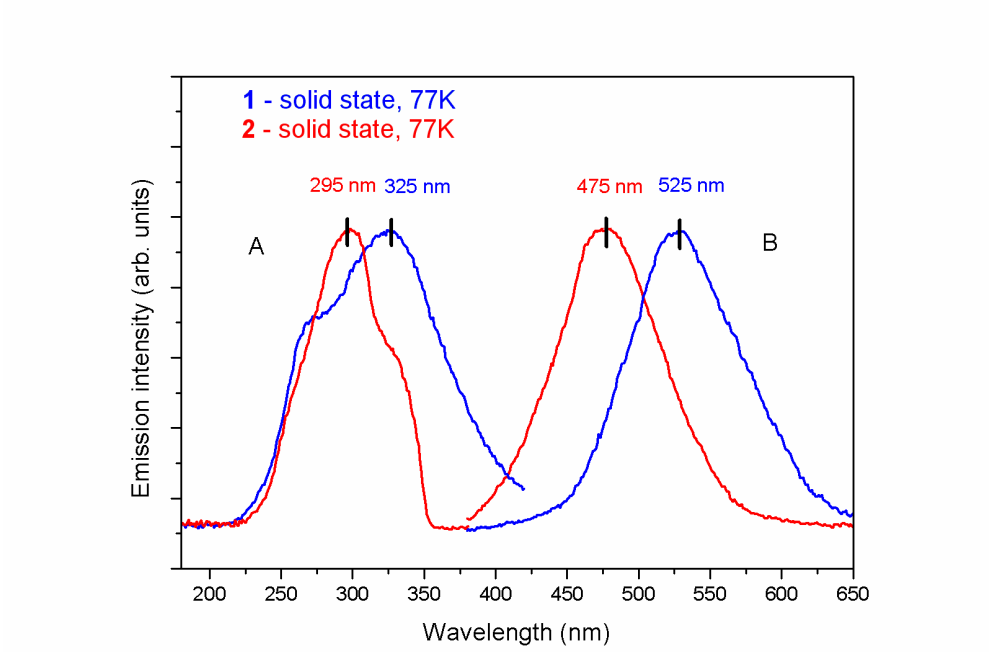

Fig. S5 Photoluminescence excitation (A) and emission (B) spectra of **1** (blue traces) and **2** (red traces) in the solid state, recorded at 77 K. λ_{exc} (**1**) = 325 nm, λ_{exc} (**2**) = 295 nm, λ_{mon} (**1**) = 525 nm, λ_{mon} (**2**) = 475 nm.

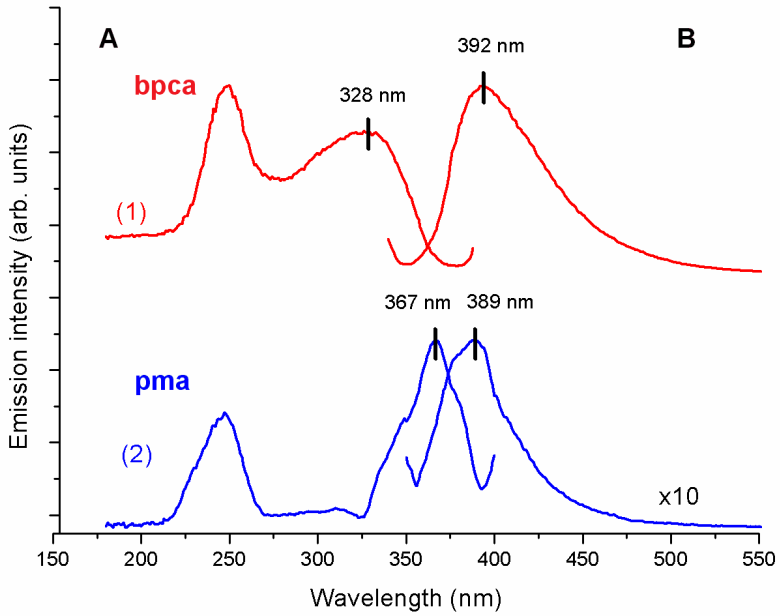

Fig. S6 Fluorescence excitation (A) and emission (B) spectra of H_2bpca (red traces) and H_4pma (blue traces) in the solid state, recorded at room temperature.

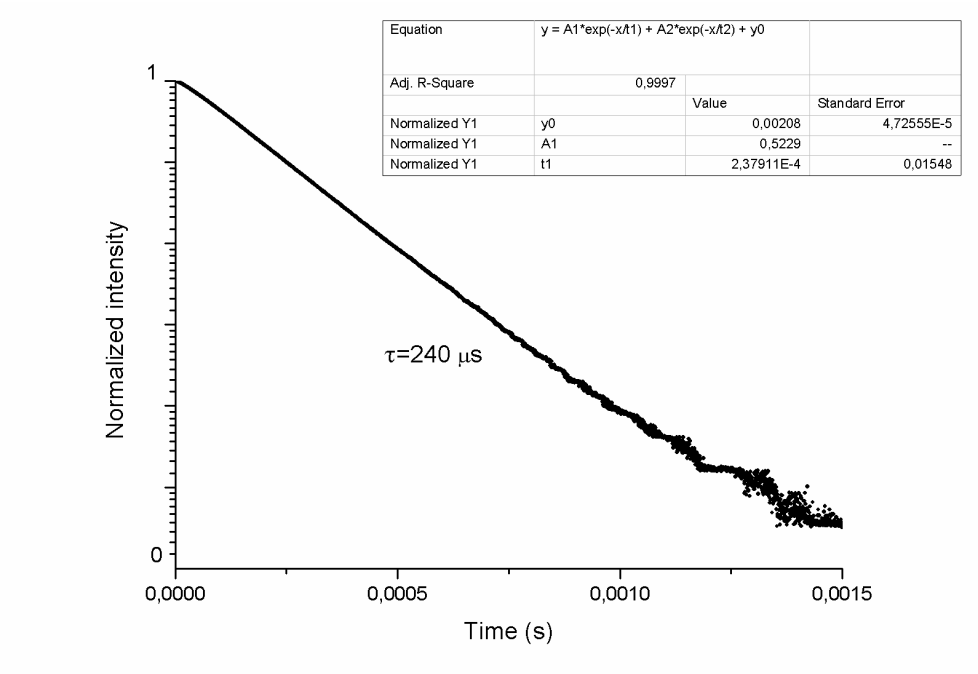

Fig. S7 Luminescence decay of **1** in the solid state measured at 77 K (λ_{exc} = 355 nm).