SUPPORTING INFORMATION

Sequential incorporation of metallic cations (Cd²⁺ and Hg²⁺) and N-Octylamine into Titanium Phosphate Nanoparticles and their subsequent release in acid media

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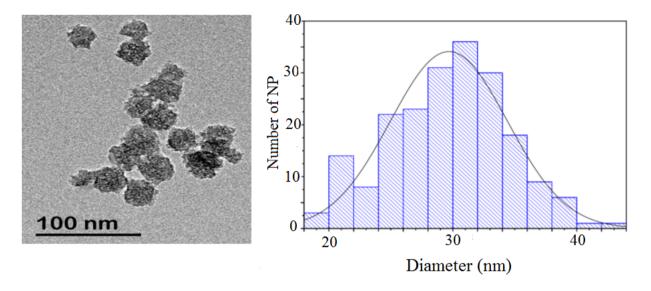


Figure S-1 TEM Micrographs (left) and Size distribution (right) of TPNP.

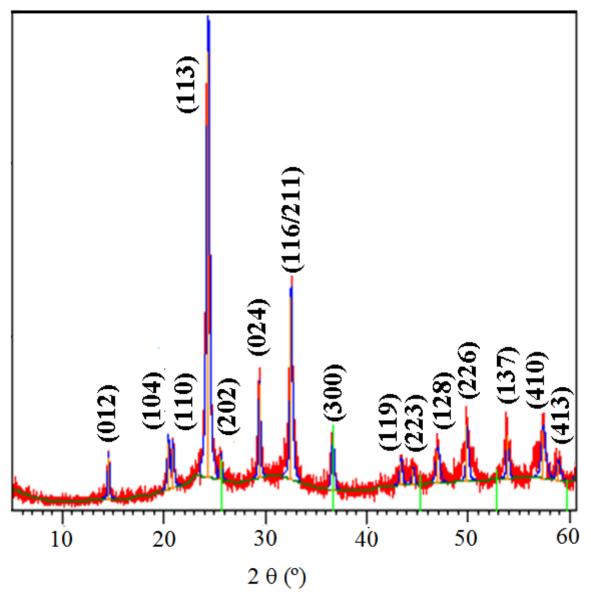


Figure S-2 XRD pattern of TPNP.

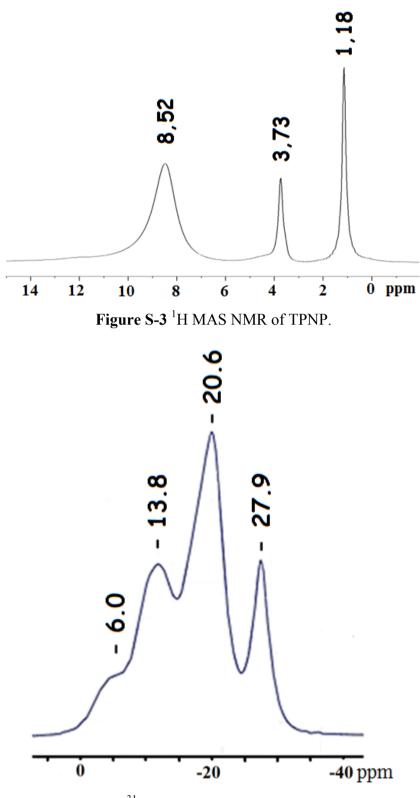


Figure S-4 ³¹P CP/MAS NMR spectrum of TPNP.

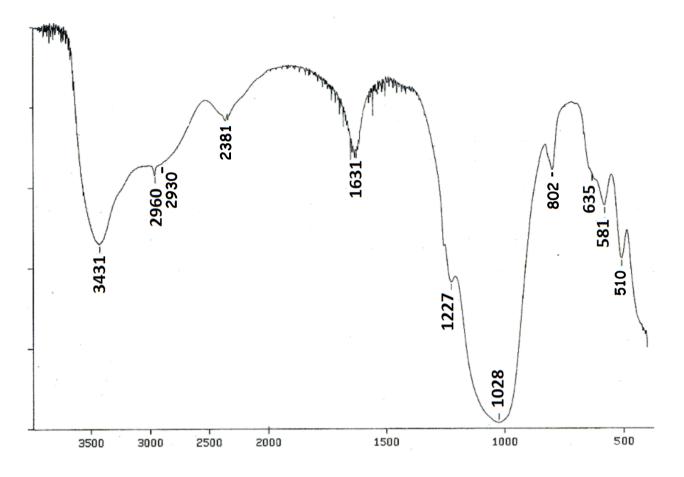


Figure S-5 Infrared spectrum of TPNP (4000-400 cm⁻¹).

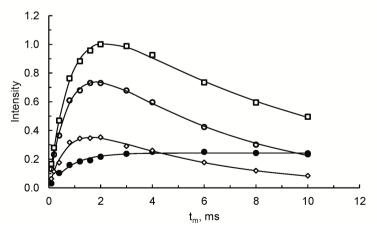


Figure S-6. ¹H \rightarrow ³¹P CP kinetics with MAS at 6 kHz in TPNP: (•) -27.9 ppm; (□) -20.6 ppm; (○) -13.8 ppm, and (◊) -6.0 ppm. The fittings use eq. $I(t) = I_0 \left(1 - \frac{T_{IS}}{T_{1\rho}^I}\right)^{-1} \left[\exp\left(-\frac{t_m}{T_{1\rho}^I}\right) - \exp\left(-\frac{t_m}{T_{IS}}\right)\right]$ where I(t) represents the peak intensity, I_0 is the absolute intensity, T_{IS} is the CP time constant between nuclei I (¹H) and S (³¹P), $T_{1\rho}^I$ is the spin-lattice relaxation time in the rotating frame of nuclei I and t_m is the contact time.

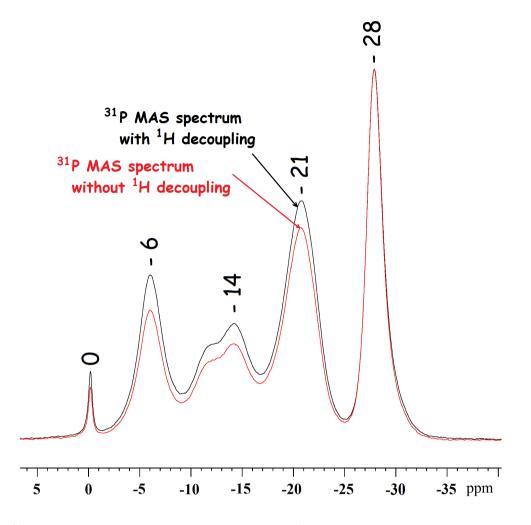


Figure S-7 ³¹P MAS NMR spectra of TPNP, one with ¹H decoupling (black), the other without ¹H decoupling (red).

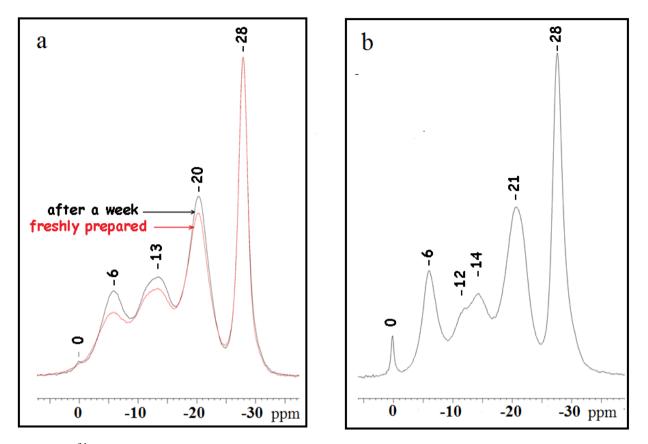


Figure S-8 ³¹P MAS NMR spectrum of TPNP freshly prepared (red) and after a week (black) (a) and after four months (b).

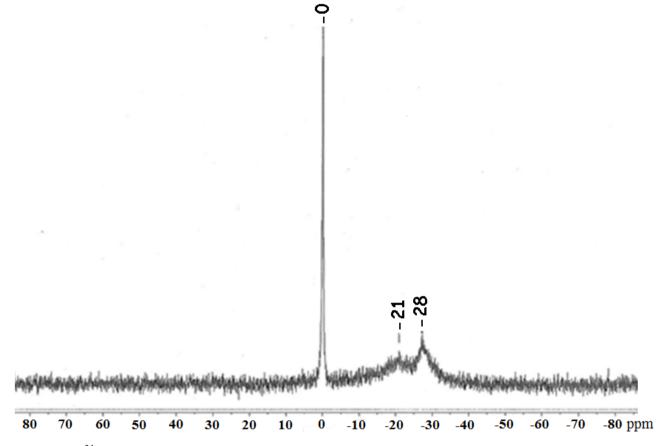


Figure S-9 ³¹P NMR spectrum of TPNP in D_2O after stirring at room temperature the nanoparticles in deuterated water for 10 minutes.

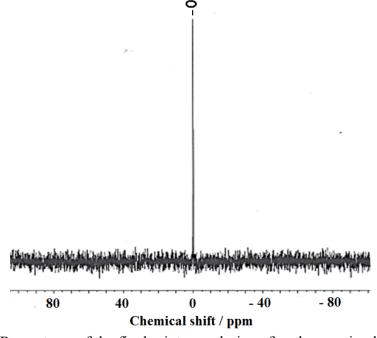


Figure S-10 ³¹P NMR spectrum of the final mixture solution after the reaction between TPNP (40 mg) and Cd(NO₃)₂ (0.17 mmol) at 50°C for 2h. Initially, the titanium phosphate nanoparticles were added to the cadmium salt solution.

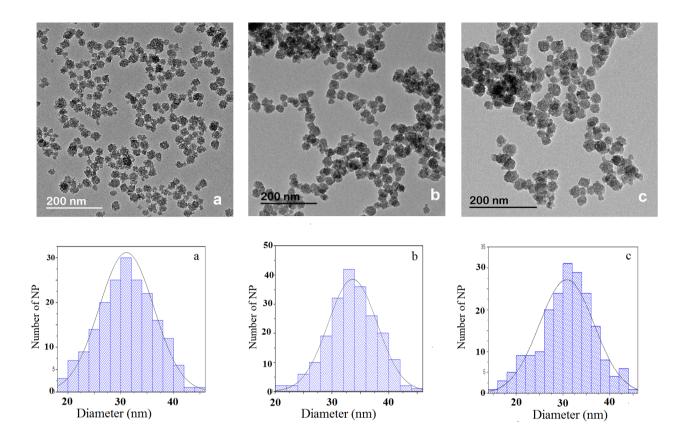


Figure S-11 TEM Micrographs (top) and Size distribution (bottom) of TPNP-Cd-1(a), TPNP-Cd-2 (b) and TPNP-Cd-3 (c).

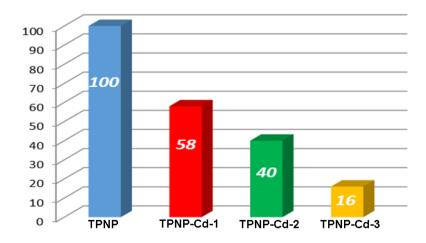


Figure S-12 Relative area under the fluorescence signal at 720 nm corresponding to TPNP, TPNP-Cd-1, TPNP-Cd-2 and TPNP-Cd-3.

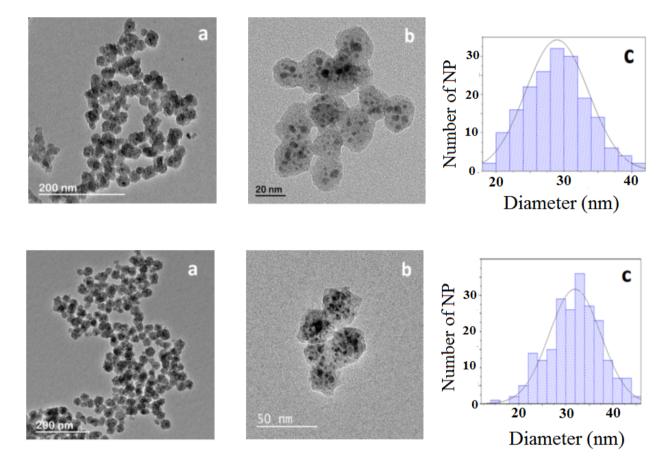


Figure S-13 Overview (a) and detailed (b) TEM Micrographs and Size distribution (c) of TPNP-Hg-1 (top) and TPNP-Hg-2 (bottom).

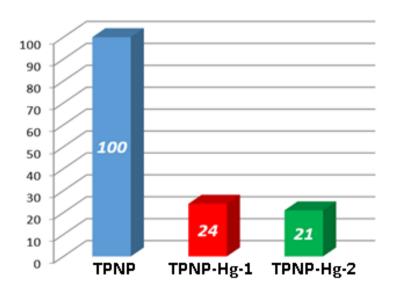


Figure S-14 Relative area under the fluorescence signal at 720 nm corresponding to TPNP, TPNP-Hg-1 and TPNP-Hg-2.

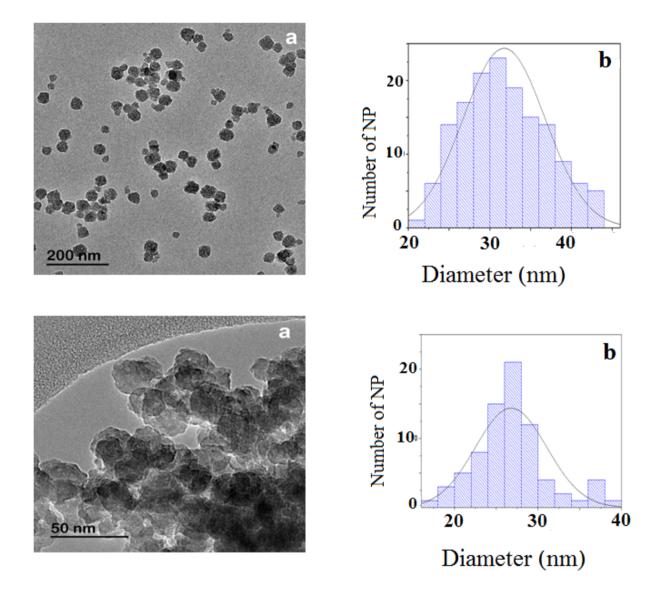


Figure S-15 TEM Micrographs (a) Size distribution (b) of TPNP-Cd-2-H (top) and TPNP-Hg-2-H (bottom).

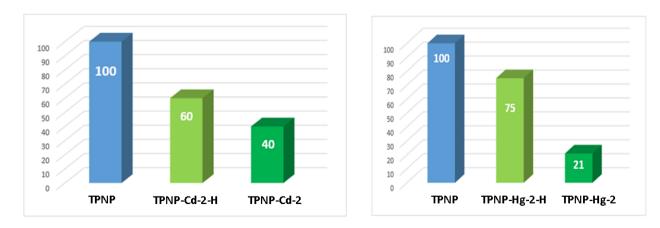


Figure S-16 Relative area under the fluorescence signal at 720 nm corresponding to TPNP, TPNP-Cd-2-H and TPNP-Cd-2 (left) and to TPNP, TPNP-Hg-2-H and TPNP-Hg-2 (right).

| $TPNP + Cd(CH_3COO)_2.2H_2O$ 40 mg 170 μ moles | 50°C, 24 h ► | TPNP-Cd-2 + Cd^{2+} in solution 80 ± 1 µmoles |
|--|--------------|--|
| TPNP-Cd-2 + HCl 0.1 M | r. t., 60 s | TPNP-Cd-2-H + Cd ²⁺ in solution $70 \pm 2 \ \mu$ moles |
| TPNP-Cd-2-H + HCl 0.1 M | r. t., 24 h | Cd^{2+} in solution 34 ± 7 µmoles |

Figure S-17 Monitoring of Cd²⁺ abundance in solution and the incorporation /release of the cadmium (II) cation to/from titanium phosphate nanoparticles.

| TPNP + Hg(CH ₃ COO) ₂ 40 mg 170 μmoles | 50°C, 24 h ► | TPNP-Hg-2 + Hg^{2+} in solution 53 ± 2 µmoles |
|--|--------------|--|
| TPNP-Hg-2 + HCl 0.1 M | r. t., 60 s | TPNP-Hg-2-H + Hg^{2+} in solution 80 ± 7 µmoles |
| TPNP-Hg-2-H + HCl 0.1 M | r. t., 24 h | Hg^{2+} in solution $27\pm5~\mu moles$ |

Figure S-18 Monitoring of Hg²⁺ abundance in solution and the incorporation/release of the mercury (II) cation to/from titanium phosphate nanoparticles.

| Phosphate group | δ _{iso} , ppm | $T_{1\rho}(^{1}H)^{a}, ms$ | T _{HP} ^a , ms |
|---------------------------------|------------------------|----------------------------|-----------------------------------|
| $(PO_4)^{3-}$ | -27.9 | ∞ | 0.83 (0.06) |
| $(\mathrm{HPO}_4)^{2-}$ | -20.6 | 9.6 (0.4) | 0.83 (0.03) |
| $({\rm H}_{2}{\rm PO}^{4})^{-}$ | -13.8 | 6.2 (0.2) | 0.78 (0.03) |
| (NaH_2PO_4) | -6.0 | 5.2 (0.4) | 0.71 (0.06) |

Table S-1. Cross-polarization time constants

^aStandard deviation shown in parenthesis.