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

An unprecedented anionic Ln-MOF with cage-within-cage motif: spontaneous reduction and immobilization of ion-exchanged Pd(II) to Pd-NPs in the framework

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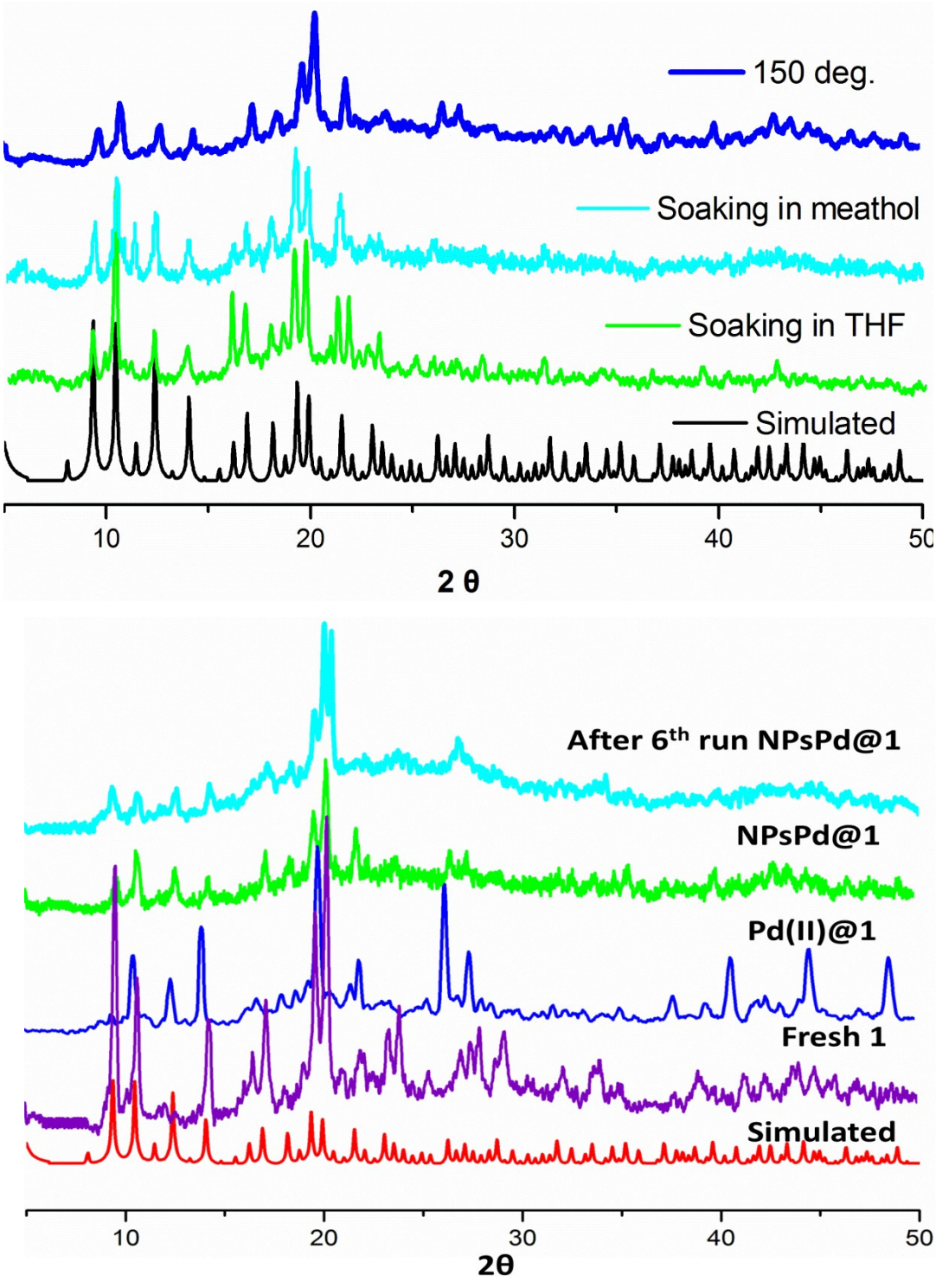


Fig. S1 The PXRD curves of **1** and the Pd^{2+}/Pd-NPs inclusion compounds.

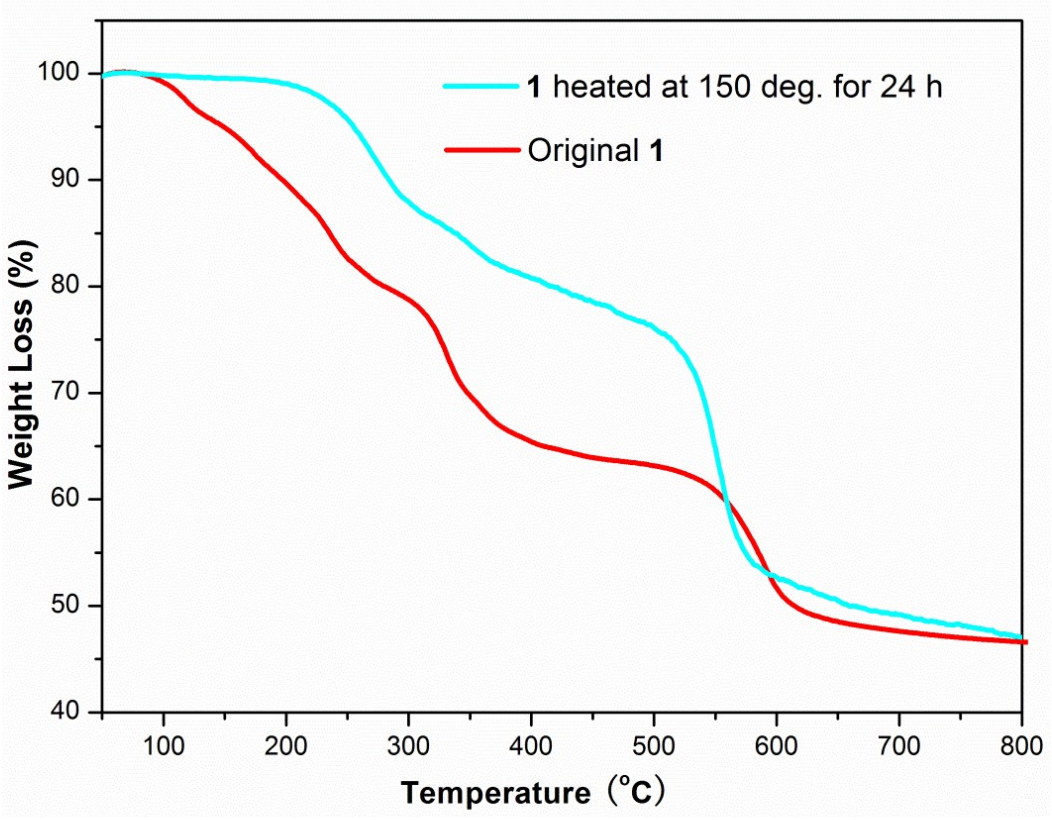


Fig. S2 TGA curves of **1** and the desolvated sample by heating **1** at 150°C for 24 h.

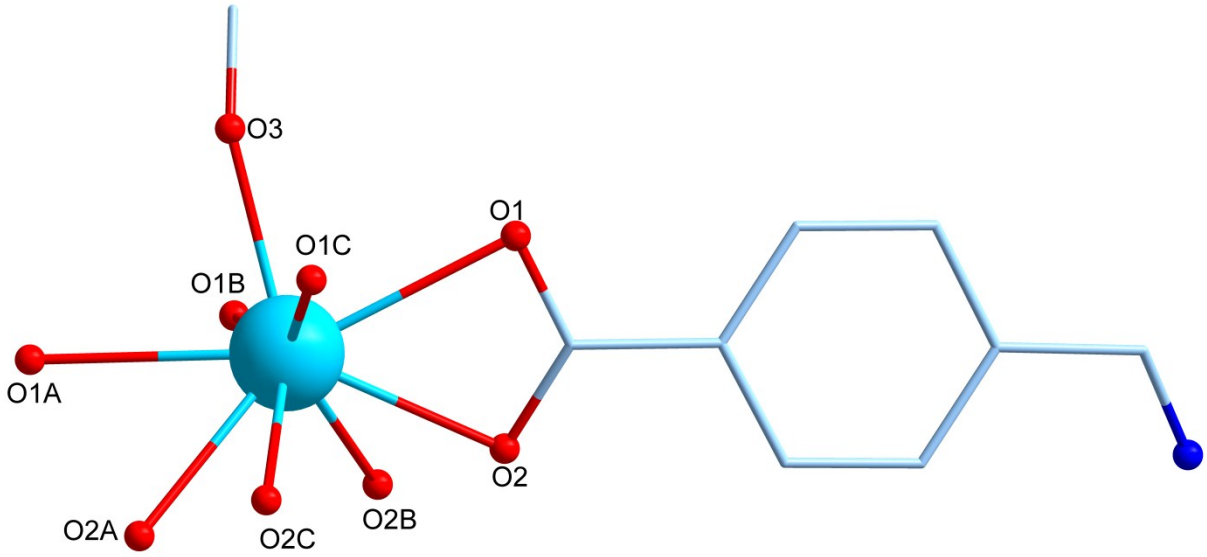


Fig. S3 The coordination environment of Tb^{3+} in **1**. Symmetry code: (A) −x, −y+1, z; (B) x, −y+1, z; (C) −x, y, z; (D) y, z, x.

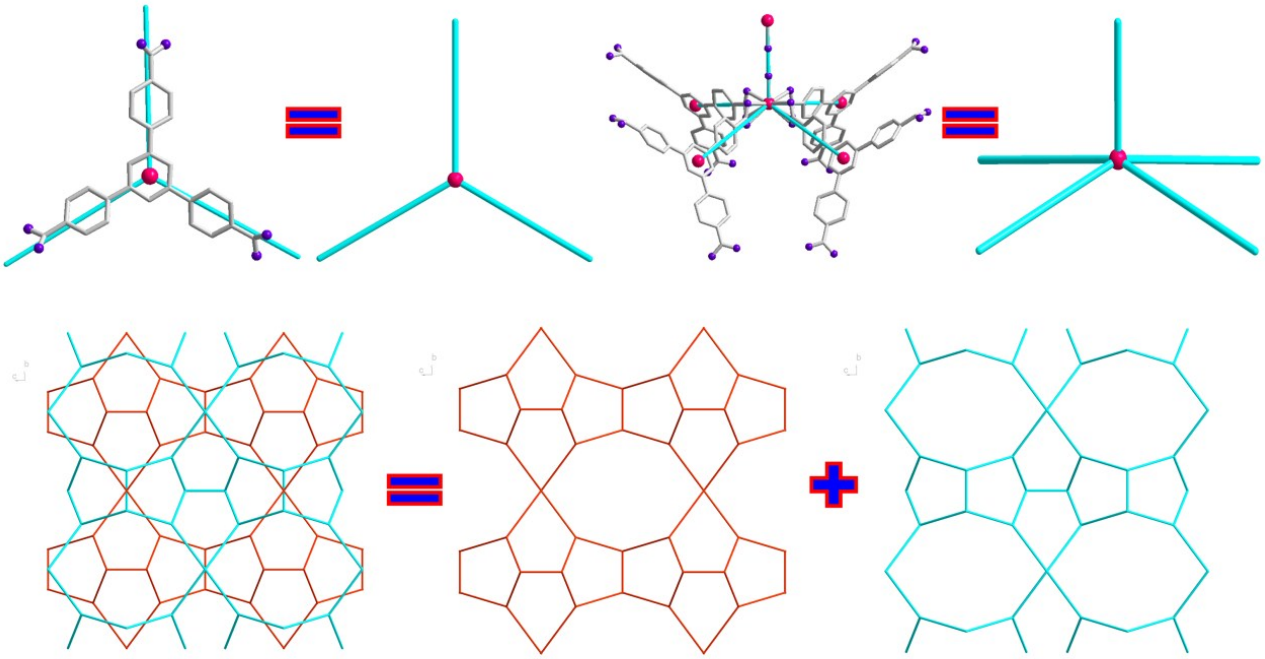
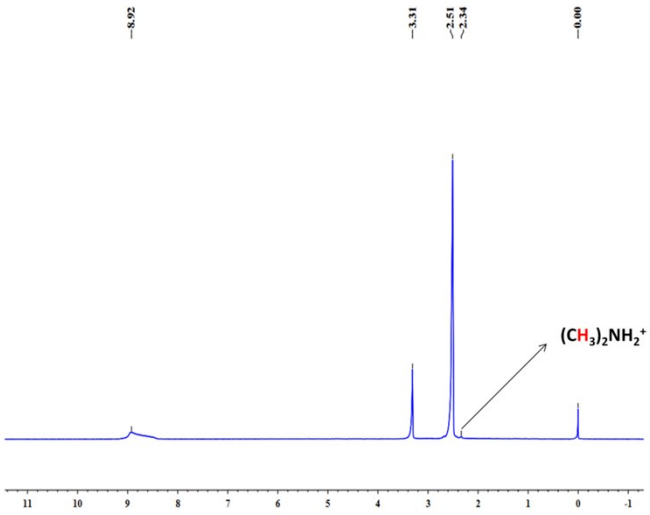
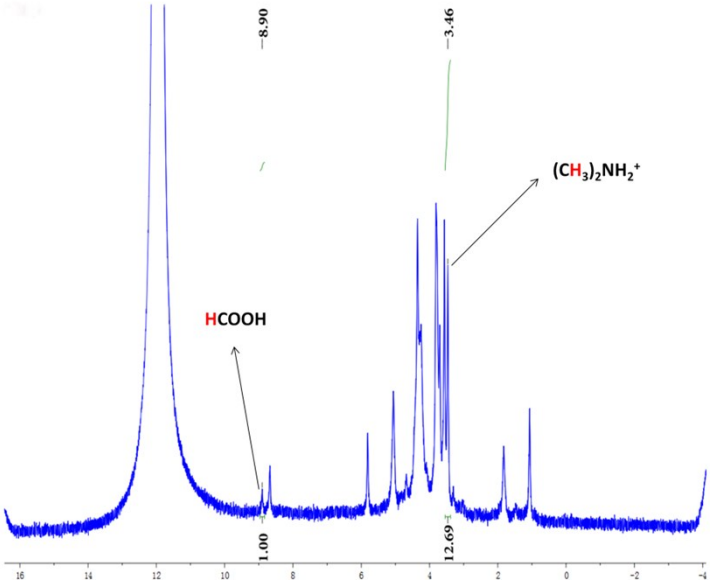


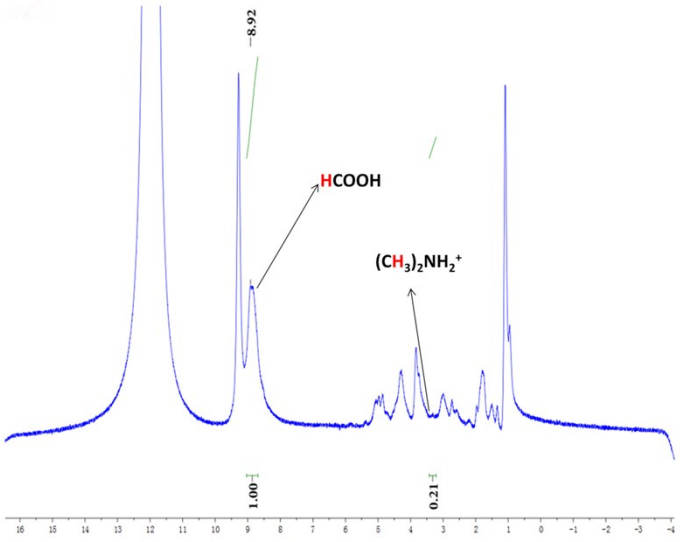
Fig. S4 The network topology of **1**.



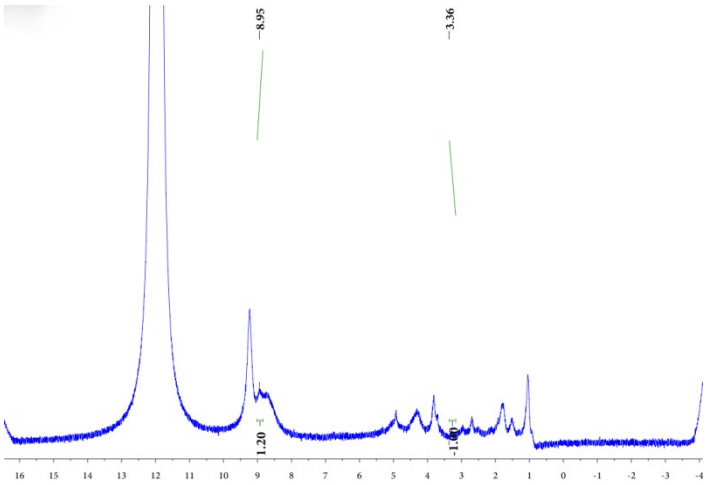
(a)



(b)



(c)



(d)

Fig. S5 (a) ^{1}H NMR spectrum of **1a** after immersed in DMSO-d6 containing Pd^{2+}, (b) ^{1}H NMR spectrum of acid-digested sample **1a**, (c) ^{1}H NMR spectrum of acid-digested sample **1c**, (d) ^{1}H NMR spectrum of acid-digested sample **Pd-NPs@1c.**

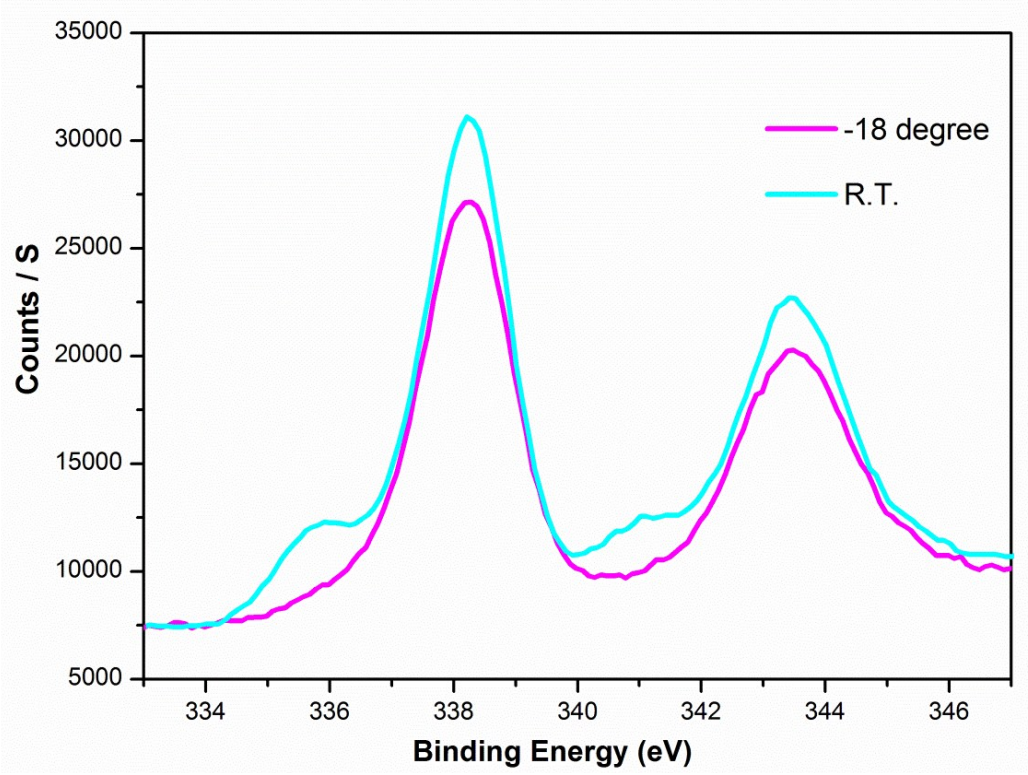


Fig. S6 X-ray photoelectron spectra of the Pd^{2+} embedded samples prepared at –18°C (Pink) and at room temperature for one day in THF (Turquoise).

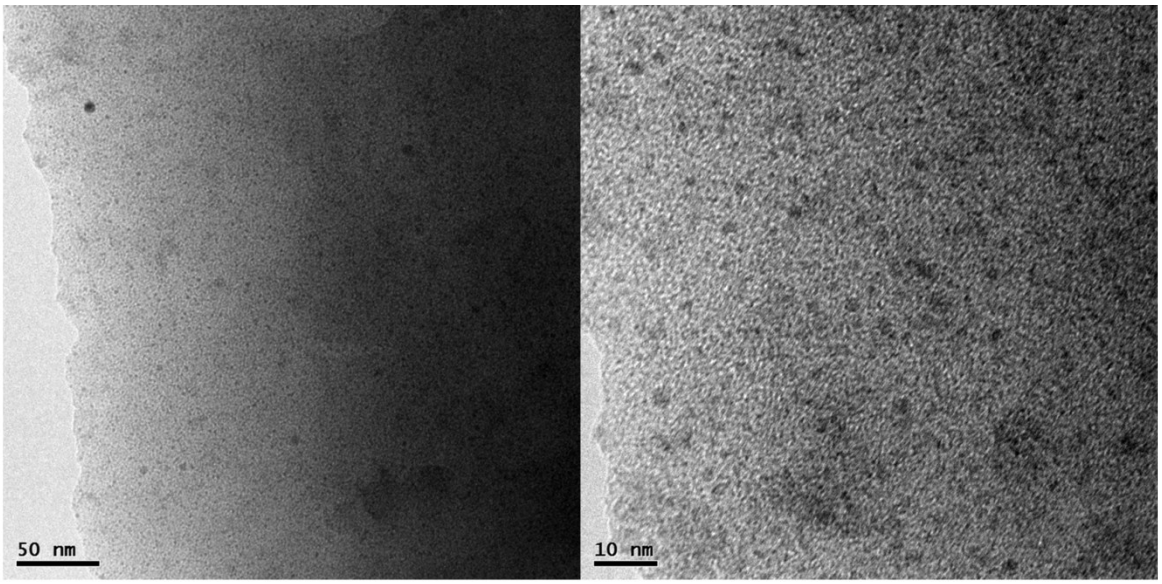


Fig. S7 TEM images of **Pd-NPs@1** *via* self-redox of **1b** in vacuum at room temperature for four weeks.

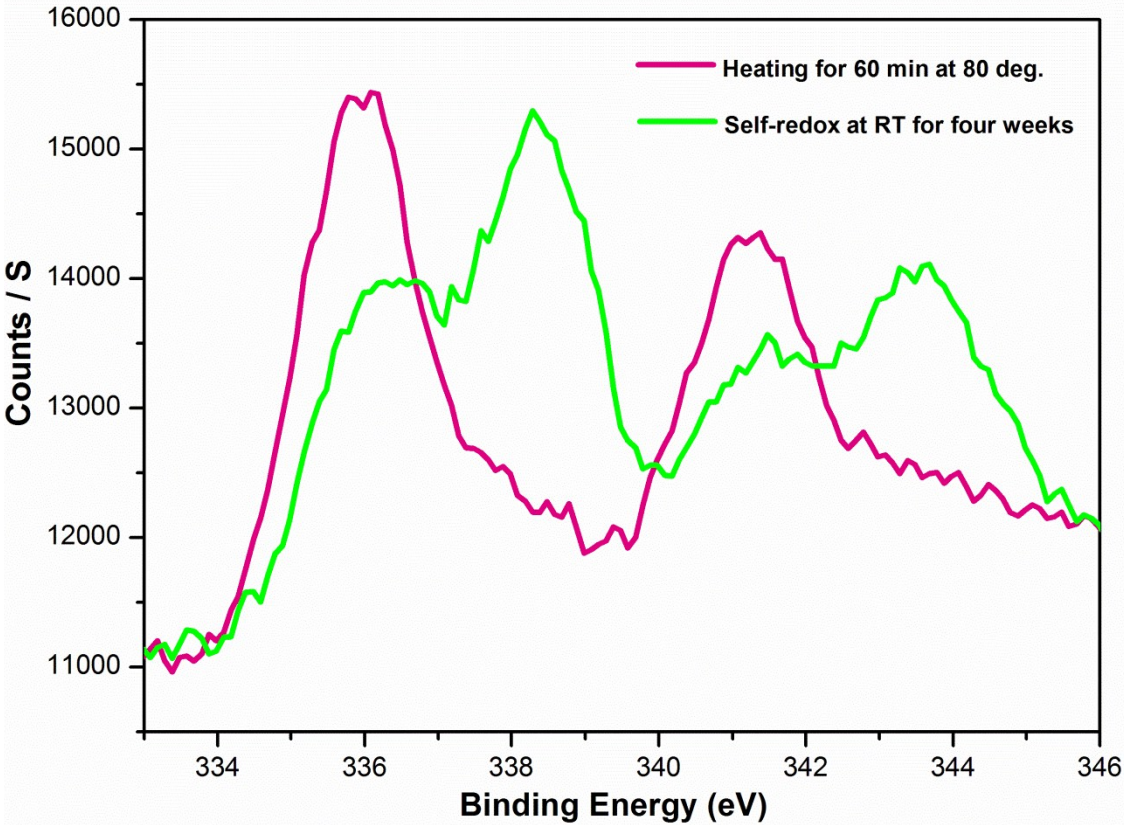


Fig. S8 X-ray photoelectron spectra of **Pd-NPs@1** prepared by heating **1b** for 1 h at 80°C in vacuum and that through self-redox of **1b** under vacuum at room temperature for four weeks.

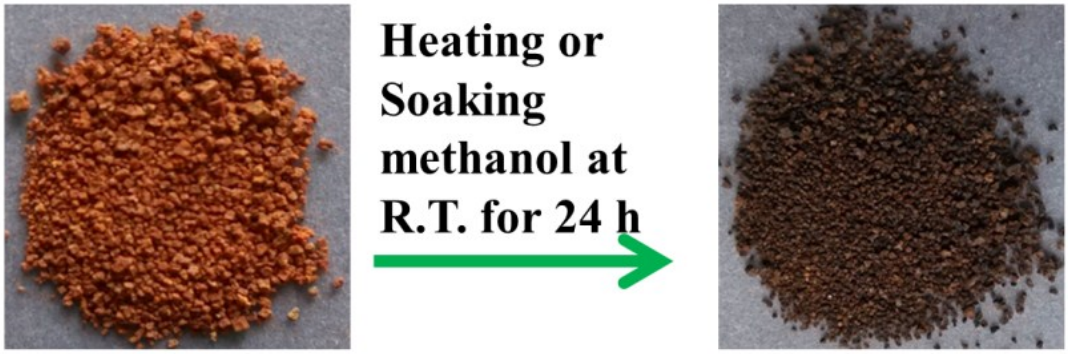


Fig. S9 The colour change from orange to black-brown with heating or soaking methanol at R.T. for 24 h.

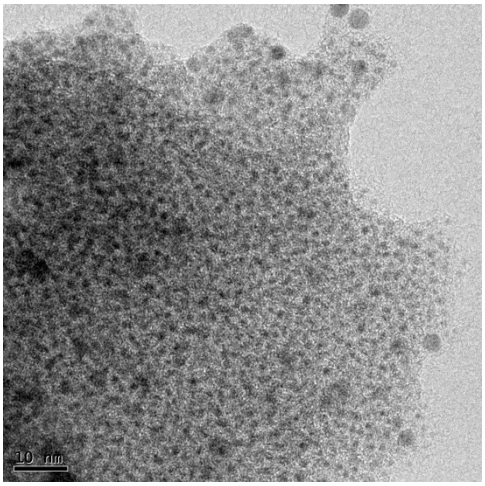


Fig. S10 TEM image of **Pd-NPs@1c**

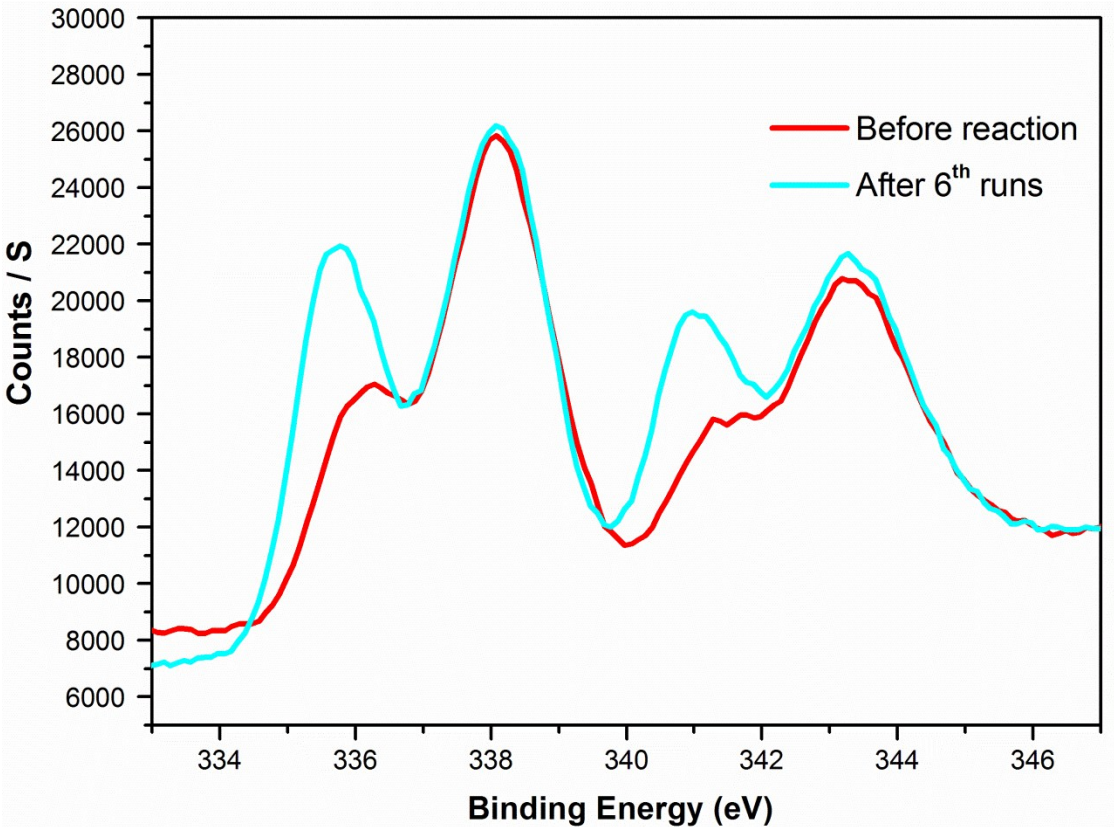


Fig. S11 X-ray photoelectron spectra of **NPsPd@1′** and **NPsPd@1′** after the 6th catalytic run.

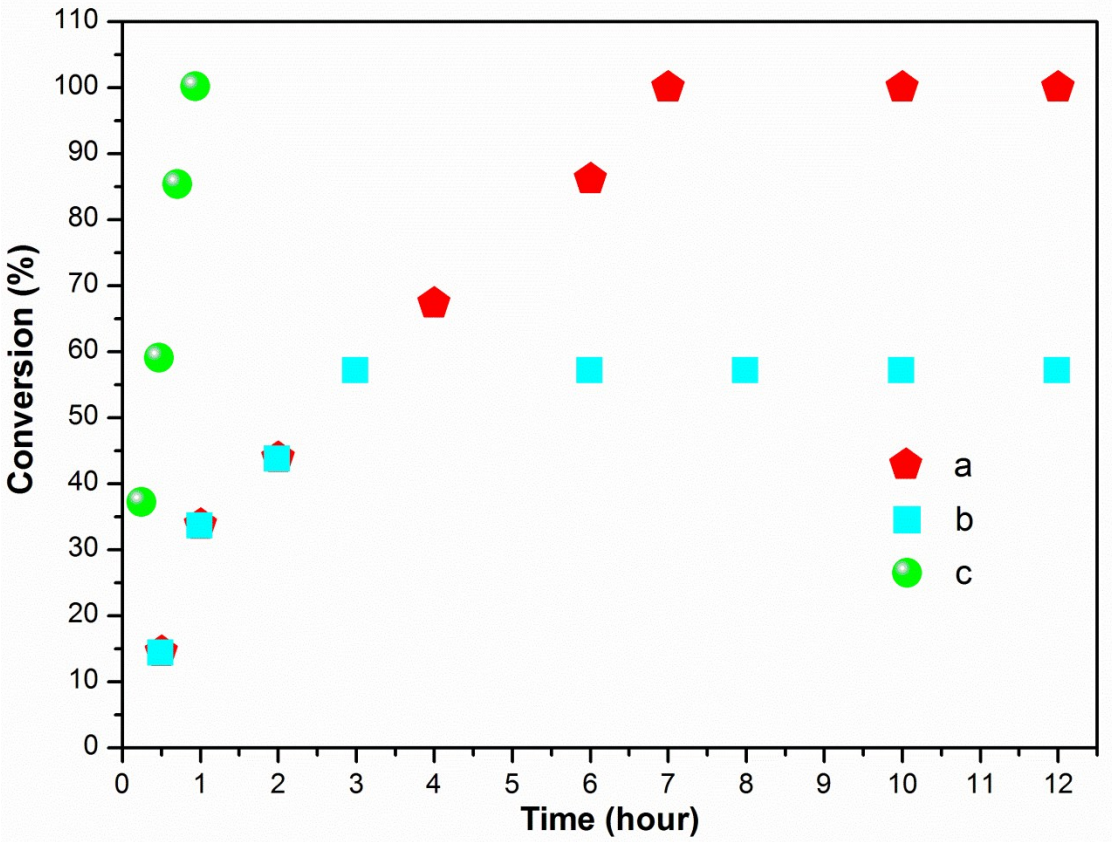


Fig. S12 (a) Time profile of the conversion of styrene to ethylbenzene catalyzed by **Pd-NPs@1** at room temperature; (b) After the reaction was performed for 3 hours, **Pd-NPs@1** was removed from the solution and the reaction was continued for another 9 hours; (c) Time profile of the conversion of styrene to ethylbenzene catalyzed by **Pd-NPs@1** at 60°C.

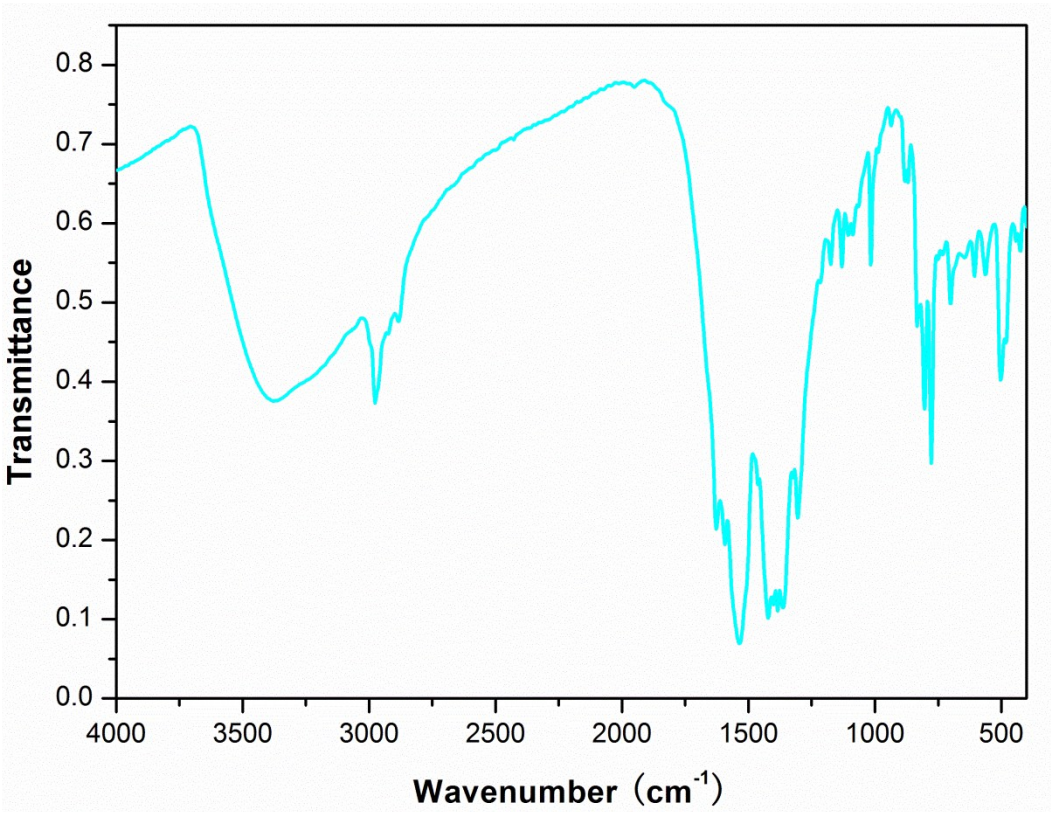


Fig. S13 The IR spectrum of **1**.

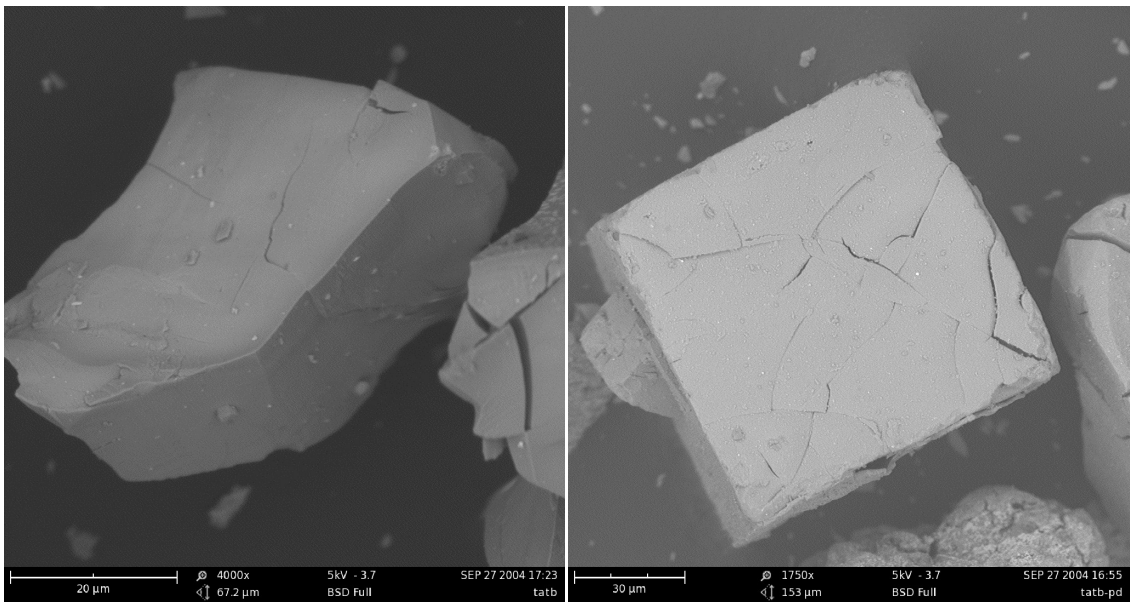
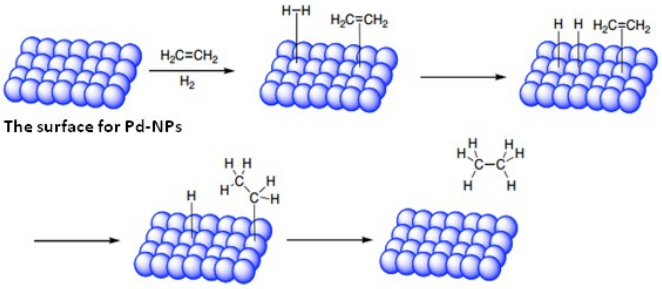


Fig. S14 The SEM images of fresh **1** (left) and Pd-NPs@**1** (right).



Scheme S1 The proposed mechanism for the hydrogenation of an alkene catalysed by Pd-NPs

Table S1 Crystallographic data and structure refinement details for **1**

Compound	**1**
Formula	$C_{480}H_{576}N_{72}O_{180}Tb_{12}$
Fw	12141.31
Cryst. Syst.	Cubic
space group	*Im-3*
a, Å	26.7264(13)
α, º	90.00
V, Å^3	19090.7(16)
Z	2
μ, mm^{-1}	1.163
D_{calcd},g cm^{-3}	1.056
GOF	1.196
$^aR_1$	0.0628
wR_2	0.1521

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$