"Click" dendrimer-Pd nanoparticle assemblies as enzyme mimics: Catalytic *o*-phenylenediamine oxidation and application to colorimetric H_2O_2 detection

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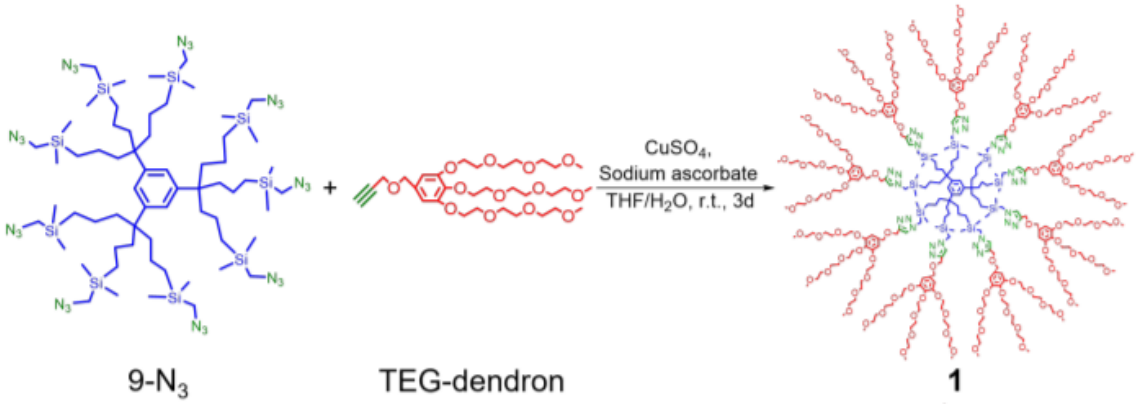
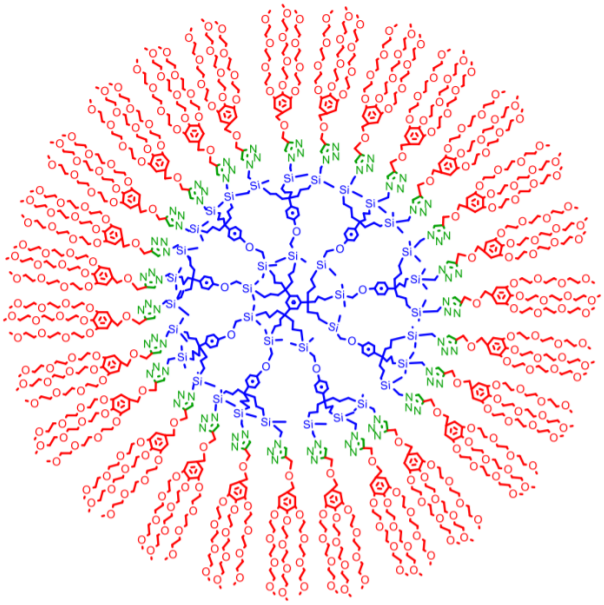
Electronic Supplementary Information (ESI)

1. Procedure for the preparations of the dendrimer-1 and dendrimer-2



Scheme 1. Synthesis of dendrimer-**1**

Dendrimer **1** has been synthesized following previous reports. [S1, S2] 1,2 9-N_3 (see Scheme 1, 0.012 mmol,) and the TEG dendron (see Scheme 1, 0.13 mmol, 1.2 equiv. per branch) are dissolved in THF. $CuSO_4.5H_2O$ is added (0.032 g, 0.13 mmol, 1.2 equiv. per branch, 1M in aqueous solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (0.051 g, 0.26 mmol, 2.4 equiv. per branch, 1M in water solution) in order to set a 1:1 THF/water ratio. The reaction mixture is stirred for 3 days at 25 °C under N_2. After removing THF in vacuo, CH_2Cl_2 (100 mL) and an aqueous ammonia solution (2.0 M, 50 mL) are successively added. The mixture is allowed to stir for 10 minutes in order to remove all the Cu(II) trapped inside the dendrimer as $[Cu(NH_3)_2(H_2O)_2][SO_4]$. The organic phase is washed twice with water, and this operation is repeated three more times to ensure complete removal of copper ions. The organic phase is dried with sodium sulfate, and the solvent is removed *in vacuo*. The product is washed with 50 mL pentane several times in order to remove the excess of the dendron. Dendrimer **1** is obtained in 72.8 % yield. The procedure for the synthesis of dendrimer **2** is similar to that used for **1**, and use the procedure reported in reference S1, **2** is obtained in 70 % yield.



Dendrimer **2**

2. ^{1}H NMR of the dendrimer-1 and dendrimer-2

^{1}H NMR ($CDCl_3$, 300 MHz) d_{ppm}: 7.51 (CH-triazole), 6.99 (CH-arom. intern), 6.60 (CH-arom. extern), 4.63 (triazole-CH_2-O), 4.48 (O-CH_2-arom. extern), 3.85-4.15 (CH_2CH_2O-arom. extern), 3.80 (Si-CH_2-triazole), 3.53-3.77 (OCH_2CH_2O), 3.37-3.40 (CH_3O), 1.70 ($CH_2CH_2CH_2Si$), 1.13 ($CH_2CH_2CH_2Si$), 0.66 ($CH_2CH_2CH_2Si$), 0.07 ($Si(CH_3)_2$).

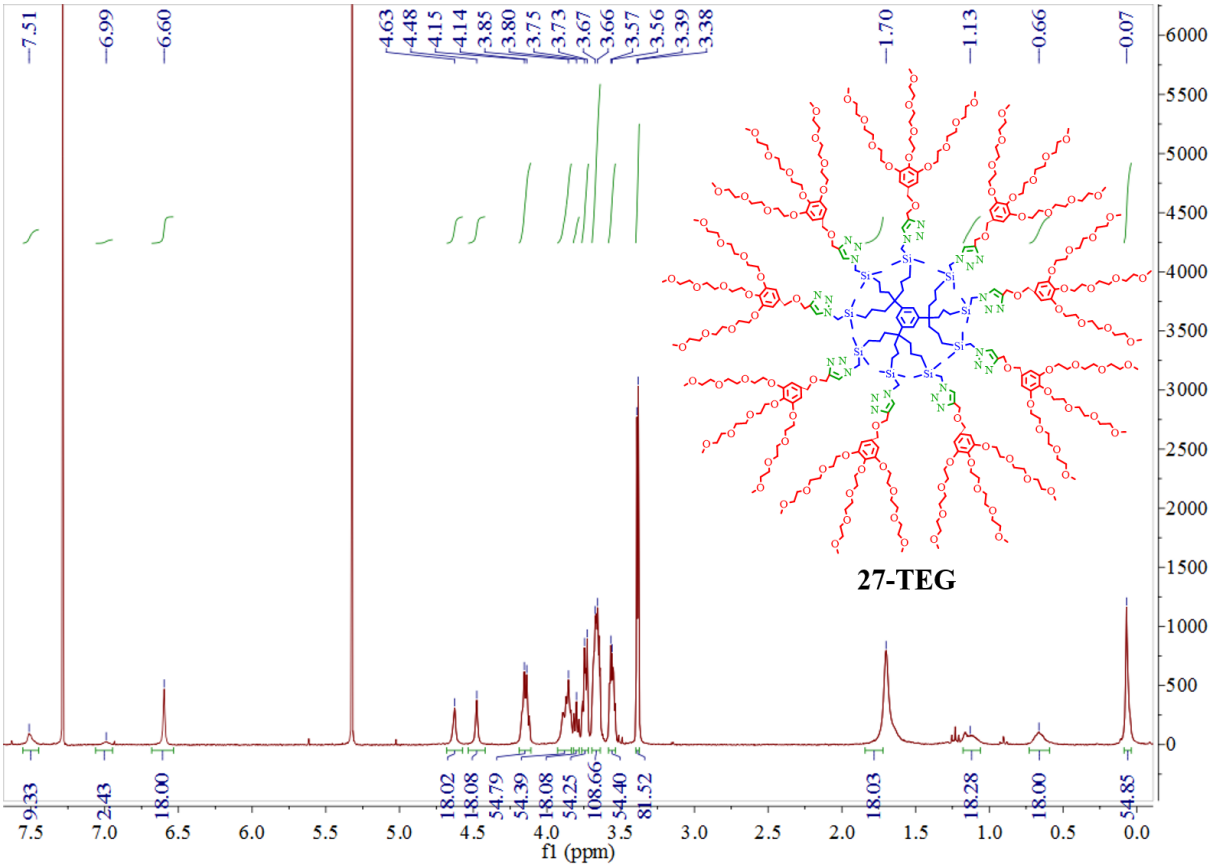


Figure S1. ^{1}H NMR spectrum of dendrimer-**1** in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 300 MHz) d_{ppm}: 7.51 (CH-triazole), 6.89-7.15 (CH-arom. intern), 6.60 (CH-arom. extern), 4.64 (triazole-CH_2-O), 4.48 (O-CH_2-arom. extern), 3.85-4.15 (CH_2CH_2O-arom. extern), 3.80 (Si-CH_2-triazole), 3.56-3.74 (OCH_2CH_2O), 3.55 (CH_2O-arom. intern) 3.36-3.40 (CH_3O), 1.63 ($CH_2CH_2CH_2Si$), 1.12 ($CH_2CH_2CH_2Si$), 0.63 ($CH_2CH_2CH_2Si$), 0.06 ($Si(CH_3)_2$).

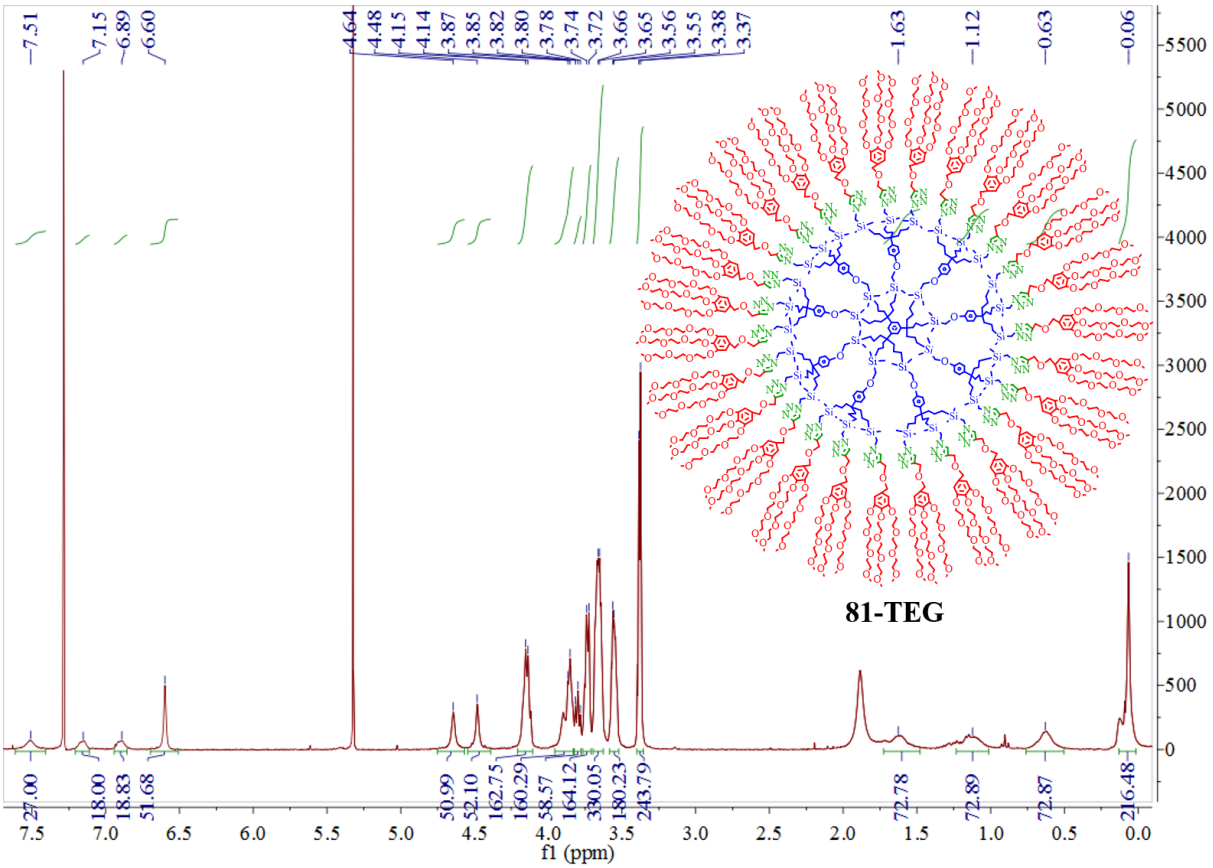


Figure S2. ^{1}H NMR spectrum of dendrimer-**2** in $CDCl_3$.

3. *XPS experiments for the dendrimer-1-PdNPs and dendrimer-2-PdNPs.*

XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Magnesium Kα line of 1253.6 eV energy and 252 W), placed perpendicular to the analyzer axis and calibrated using the $3d_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 1.1 eV.

3.1 Carbon 1s region of the dendrimer-1-PdNPs and dendrimer-2-PdNPs.

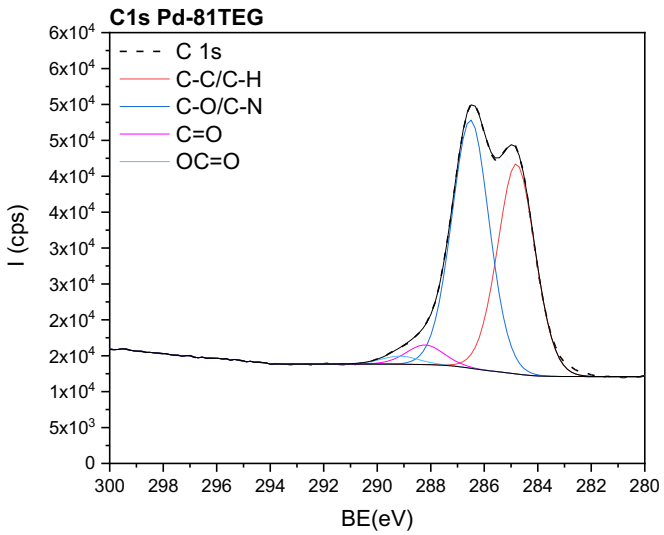


Figure S3. Carbon 1s region of dendrimer-**2**-PdNPs

Table S1 C 1s peak BE obtained by deconvolution and reported in Figure S3 and Figure S4.

	C-C/C-H (eV) [at%]	**C-O/C-N (eV) [at%]**	**C=O (eV) [at%]**	**OC=O (eV) [at%]**
Pd-27TEG	284.8 [61.2]	286.4 [32.3]	288.2 [4.2]	289.3 [2.3]
Pd-81TEG	284.8 [43.2]	286.5 [51.1]	288.2 [4.0]	289.2 [1.7]

3.2 Oxygen 1s region of the dendrimer-1-PdNPs and dendrimer-2-PdNPs.

The oxygen peak is generally wide and difficult to resolve discrimination of the different species. In the literature, the O-Metal bond is <530eV, C=O 530-531 eV, C-O and Si-O 531-533 eV, OC=O and C-OH and H_2O >534eV. Pd $3p_{3/2}$ BE can vary from 532 (Pd^0) eV up to 535 eV ($PdCl_2$).

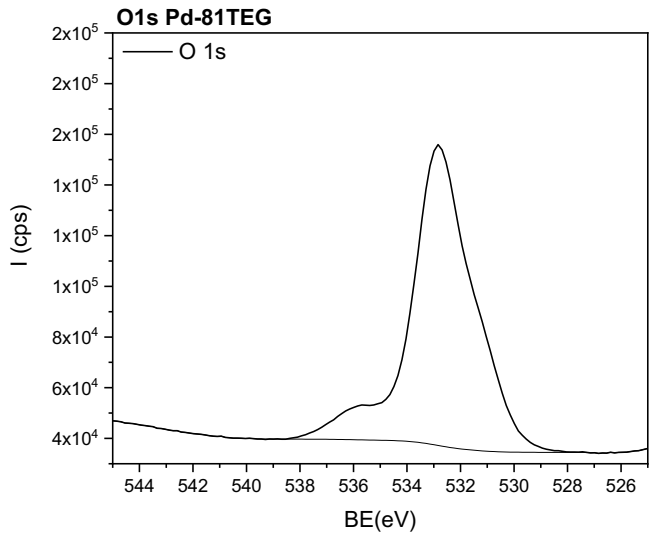


Figure S4. Oxygen 1s region of dendrimer-**2**-PdNPs

3.3 Nitrogen 1s region of the dendrimer-1-PdNPs and dendrimer-2-PdNPs.

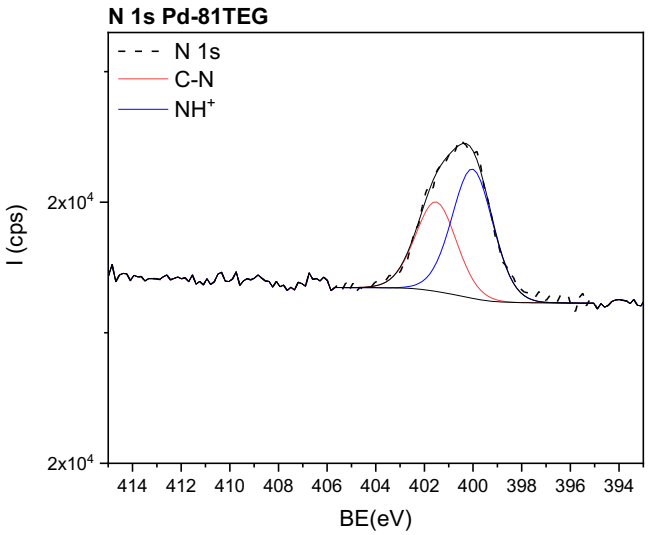


Figure S5. Nitrogen 1s region of dendrimer-**2**-PdNPs

Table S2 N 1s peak BE obtained by deconvolution and reported in Figure S7 and Figure S8.

	N-C **(eV)** **[at%]**	**NH^+** **(eV)** **[at%]**
Pd-27TEG	400.4 [100]	-
Pd-81TEG	400.0 [59]	401.5 [41]

3.4 Pd 3d region of the dendrimer-1-PdNPs and dendrimer-2-PdNPs.

Pd is readily reduced by X-ray and for this reason the acquisition time was reduced to minimum. The 3d region is represented by a doublet with average splitting of 5.3eV. Pd $3d_{5/2}$ is found below 335 eV in Pd^0 while Pd^{II} has higher BE. Several species, most likely made of Pd^{II}, were detected and indicated as (I) and (II).

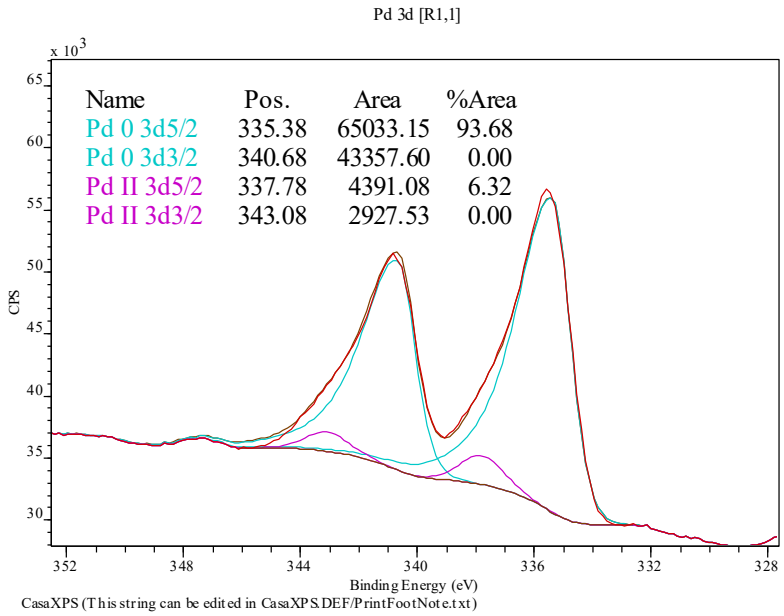


Figure S6. Pd 3d region of dendrimer-**2**-PdNPs

4. *OPD oxidation catalyzed by dendrimer-1-PdNPs at various pH values.*

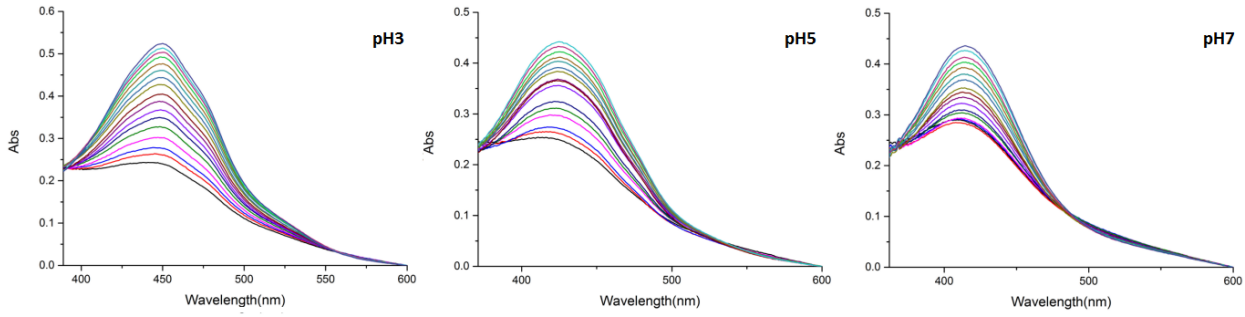


Fig. S7. OPD oxidation catalyzed by dendrimer-**1**-PdNPs at various pH.

General conditions: 0.1M OPD; 0.4 mL H_2O_2 30%; 2 mM dendrimer-**1**-PdNPs

5. *Variation of OPD concentration*

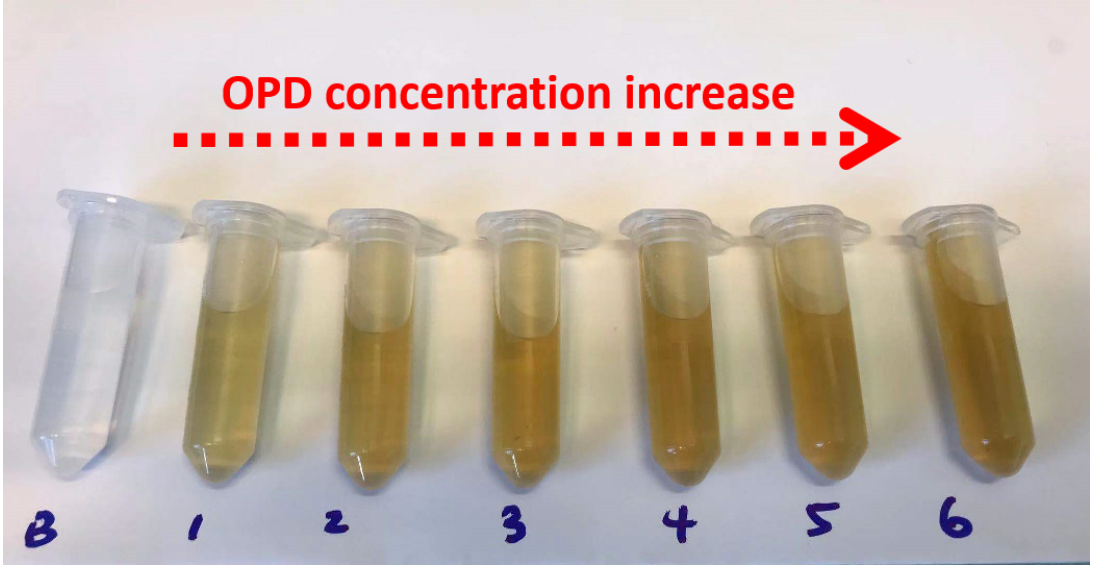


Fig. S8. Color changes during oxidization of OPD catalyzed by dendrimer-**1**-PdNPs in the presence of OPD with increased concentrations.

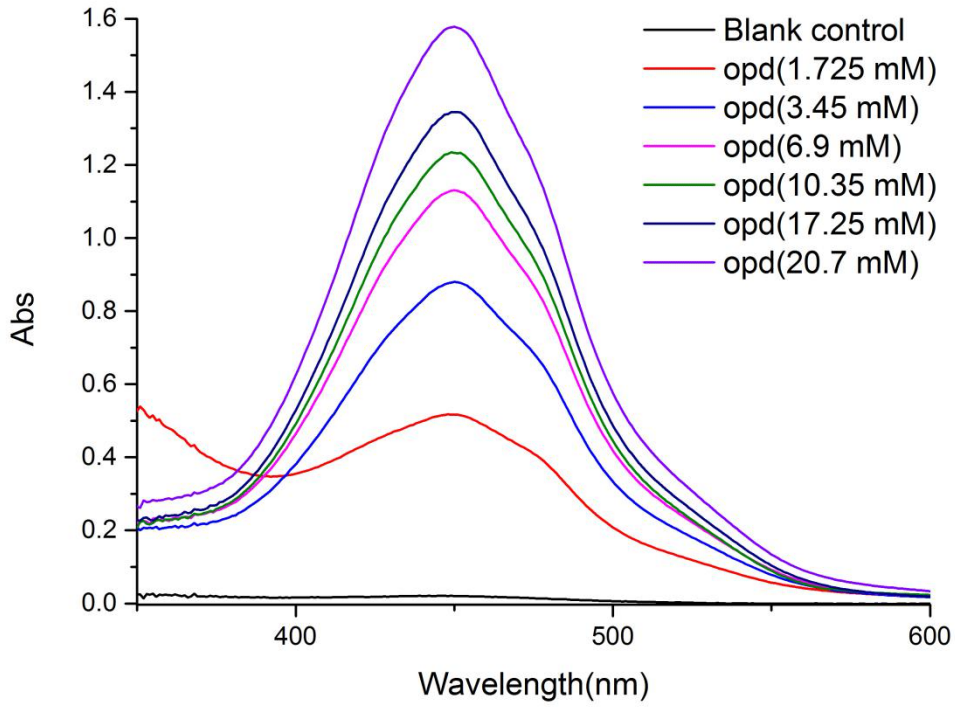


Fig. S9. Variation of OPD concentration during the catalytic oxidation by dendrimer-**1**-PdNPs.

General conditions: 0.4 mL H_2O_2 30%; 2 mM dendrimer-**1**-PdNPs

Table S3. Comparison of the apparent Michaelis–Menten constant (K_m) and maximum reaction rate (V_m) for OPD as substrate

Material	C_{H2O2}	C_{cat}	$V_{max}\times10^{-8}$ (M s^{-1})	K_m (mM)	**Ref.**
$MnFe_2O_4$	60 mM	0.06mg mL^{-1}	10.4	27.5	3
Cu-based carbon dots (Cu-CDs)	0.625 mM	0.05mg mL^{-1}	3.315	0.548	4
Co_3O_4	0.67 mM	0.05 nM	3.22	0.61	5
Fe_3O_4@Cu@Cu_2O	2.0 mM	0.05mg mL^{-1}	13.1	0.85	**6**
Horseradish peroxidase	0.625 mM	0.05mg mL^{-1}	0.12	1.8	4
dendrimer-1-PdNPs	0.4 mL	2 mM	0.149	3.02	This work

References

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