

## Electronic Supporting information

### Peptide-based surface modified silica particles: adsorption materials for dye-loaded wastewater treatment

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## Experimental

### Reagents and materials

L-Tyrosine, L-Phenylalanine, Aib (2-amino isobutyric acid), L-Lysine, D-Tyrosine and L-Alanine were purchased from Wako (Osaka, Japan). Dicyclohexyl carbodiimide (DCC) was purchased from Wako chemicals, Japan. Fluorenylmethoxycarbonyl chloride (Fmoc-Cl) was purchased from Sigma Aldrich, USA. HOBt was purchased from Dojindo chemicals, Japan. YMC silica (SIL-120-S5) having diameter 5 $\mu$ m, pore size 12 nm and surface area 300m<sup>2</sup> g<sup>-1</sup> (YMC-gel, Kyoto, Japan) was used for modification. Diethylcyanophosphanoate (DEPC) was obtained from Tokyo Chemical Industry (TCI), Japan. 3-Aminopropyltrimethoxysilane (APS) as an initiator was purchased from Chisso, Japan. Congo red dye was obtained from Sigma Aldrich, USA. Methyl orange, Ethidium bromide, Crystal Violet and Neutral red were purchased from Tokyo Chemical Industry (TCI), Japan.

#### (A) Synthesis of Sil-YAY

##### Immobilization of APS on silica surface (Sil-APS)

3-aminopropyltrimethoxysilane (APS) grafted silica was prepared by refluxing porous silica gel (3.0 g) and (1.5 ml) APS in toluene for 24 hr. After successive washing with toluene, ethanol and diethyl ether the particles were dried in vacuum. The dried particles were characterized by elemental analysis.

##### Synthesis of Tripeptide Boc-YAY-OH

###### a) Boc-Tyr(1)-OH (1)

A solution of tyrosine 9.05 g (50 mmol) in a mixture of dioxan (100 mL), water (50 mL) and 1M NaOH (50 mL) was stirred and cooled in an ice-water bath. Di-*tert*-butylpyrocarbonate 10.4 g (52 mmol) was added and stirring was continued at room temperature for 6 hrs. Then the solution was concentrated *in vacuo* to about 15 to 20 mL, cooled in an ice-water bath, covered with a layer of ethyl-acetate (about 100 mL) and acidified with a dilute solution of KHSO<sub>4</sub> to pH 2-3 (Congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The pure material was obtained.

Yield = 11.2 g (40 mmol, 80%). (Found: C, 59.47; H, 6.52; N, 4.7%. C<sub>14</sub>H<sub>19</sub>NO<sub>5</sub> (281) requires: C, 59.78; H, 6.76; N, 4.98%).

#### **b) Boc-Tyr(1)-Ala(2)-OMe (2)**

9.85 g (35 mmol) of Boc-Tyr(1)-OH was dissolved in a mixture of 20 mL dichloromethane (DCM) in an ice-water bath. H-Ala-OMe was isolated from 7.21 g (70 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentration to 10 mL and this was added to the reaction mixture, followed immediately by 7.21 g (35 mmol) of di-cyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 hrs. DCM was evaporated, residue was taken in ethyl acetate (60 mL), and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2M HCl (3 × 50 mL), brine (2 × 50 mL), 1M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) respectively. Then dried over anhydrous sodium sulfate, and evaporated *in vacuo* to yield 2 as a solid sample.

Yield = 8.9 g (24.5 mmol, 70%). (Found: C, 58.98; H, 7.2; N, 7.49%.  $C_{18}H_{26}N_2O_6$  (366) requires: C, 59.01 H, 7.10; N, 7.65%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.98-6.96 (ring Hs of Tyr, 2H, d,  $J = 8$ Hz); 6.72-6.68 (ring Hs of Tyr, 2H, m); 6.39-6.37 (Ala NH, 1H, d,  $J = 8$ Hz); 4.98-4.96 (Tyr NH, 1H, d,  $J = 8$ Hz); 4.36-4.32 ( $C^\alpha$ H of Tyr, 1H, m); 4.25 ( $C^\alpha$ H of Ala, 1H, m); 3.73 (-OCH<sub>3</sub>, 3H, s); 2.95-2.93 ( $C^\beta$ Hs of Tyr, 2H, m); 2.90-2.86( $C^\beta$ H of Ala, 1H, m); 1.42 (Boc-CH<sub>3</sub>s, 9H, s).

### c) Boc-Tyr(1)-Ala(2)-OH (3)

To 8.05 g (22 mmol) of Boc-Tyr(1)-Ala(2)-OMe, 30 mL MeOH and 20 mL of 2M NaOH were added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under *vacuo*, the residue was taken in 50 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated *in vacuo* to yield 3 as a solid compound.

Yield = 4.6 g (13 mmol, 60%). Found: C, 57.72; H, 6.61; N, 7.63%.  $C_{17}H_{24}N_2O_6$  (352) requires C, 57.95, H, 6.81, N, 7.95%.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.93-7.91 (Phenolic OH of Tyr(1), 1H, d,  $J = 8$ Hz); 6.84-6.82 (Tyr(2) NH, 1H, d,  $J = 8$ Hz); 6.24-6.22 (Ala NH, 1H, d,); 4.14-4.12 (Tyr(1) NH, 1H, d,  $J = 8$ Hz); 4.05-3.99 ( $C^\alpha$ H of Tyr(1) and  $C^\alpha$ H of Ala, 2H, m); 2.85-2.80 ( $C^\beta$ Hs of Tyr(1), 2H and  $C^\beta$ H of Ala, 2H, m); 1.32 (Boc-CH<sub>3</sub>s, 9H, s).

### d) Boc-Tyr(1)-Ala(2)-Tyr(3)-OMe (4)

4.2 g (12 mmol) of Boc-Tyr(1)-Ala(2)-OH in 10 mL of DMF was cooled in an ice-water bath and H-Tyr-OMe was isolated from 4.68 g (24 mmol) of the corresponding methyl ester

hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentration to 10 mL and it was added to the reaction mixture, followed immediately by 2.47 g (12 mmol) DCC and 1.62 g (12 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 2M HCl (3 × 50 mL), brine (2 × 50 mL), 1M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) respectively. Then dried over anhydrous sodium sulfate and evaporated *in vacuo* to yield peptide 4 as yellowish-white solid.

Yield = 5.0 g (9.5 mmol, 80%). (Found: C, 61.2; H, 6.58; N, 7.83%.  $C_{27}H_{35}N_3O_8$  (529) requires C, 61.24; H, 6.61; N, 7.93%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.99-6.97 (ring Hs of Tyr(3), 2H, d,  $J = 8$ Hz); 6.92-6.92 (ring Hs of Tyr(1), 2H, d,  $J = 8$ Hz); 6.72-6.68 (ring Hs of Tyr(1) and Tyr(3), 4H, m); 6.46-6.43 (Tyr(3) NH, 1H, d,  $J = 12$ Hz); 6.39-6.37 (Ala NH, 1H, d,  $J = 8$ Hz); 4.98-4.96 (Tyr(1) NH, 1H, d,  $J = 8$ Hz); 4.80-4.75 ( $C^\alpha$ H of Tyr(3), 1H, m); 4.36-4.32 ( $C^\alpha$ H of Tyr(1), 1H, m); 4.25 ( $C^\alpha$ H of Ala, 1H, m); 3.73 (-OCH<sub>3</sub>, 3H, s); 3.14-3.09 ( $C^\beta$ Hs of Tyr(3), 2H, m); 2.95-2.93 ( $C^\beta$ Hs of Tyr(1), 2H, m); 2.90-2.86 ( $C^\beta$ H of Ala, 1H, m); 1.42 (Boc-CH<sub>3</sub>s, 9H, s). ESI-HR-Mass  $[M+Na]^+ = 552.60$ ,  $[M+K]^+ = 567.75$ ,  $M_{[Calcd]} = 529$ . FT-IR (KBr) 3332, 2986, 2938, 1760, 1683, 1656, 1518, 1448  $cm^{-1}$ .

#### e) Boc-Tyr(1)-Ala(2)-Tyr(3)-OH (5)

To 4.76 g (9 mmol) of Boc-Tyr(1)-Ala(2)-Tyr(3)-OMe, 30 mL MeOH and 20 mL of 2M NaOH were added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under *vacuo*, the residue was taken in 50 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3 × 50 mL). The

extracts were pooled, dried over anhydrous sodium sulfate, and evaporated *in vacuo* to yield 5 as a solid compound.

Yield = 3.01 g (5.9 mmol, 65%). Found: C, 60.36; H, 6.21; N, 8.03%.  $C_{26}H_{33}N_3O_8$  (515) requires C, 60.58, H, 6.40, N, 8.15%.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.27 (-COOH, 1H, b), 8.01 (Phenolic OH of Tyr(3), 1H, d), 7.94-7.92 (Phenolic OH of Tyr(1), 1H, d,  $J = 8$ Hz); 6.99-6.89 (ring Hs of Tyr(3) and Tyr (1), 4H, m); 6.85-6.83 (Tyr(3) NH, 1H, d,  $J = 8$ Hz); 6.68-6.62 (ring Hs of Tyr(3) and Tyr(1), 4H, m); 6.24-6.22 (Ala NH, 1H, d,  $J = 8$ Hz); 4.29 ( $C^\alpha$ H of Tyr(3), 1H, m); 4.13 (Tyr(1) NH, 1H, d); 4.05-3.99 ( $C^\alpha$ H of Tyr(1) and  $C^\alpha$ H of Ala, 2H, m); 2.94-2.91 ( $C^\beta$ Hs of Tyr(3), 2H, m); 2.85-2.80 ( $C^\beta$ Hs of Tyr(1), 2H, m and  $C^\beta$ H of Ala, 1H, m); 1.30 (Boc- $CH_3$ s, 9H, s).  $C^{13}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  173.07, 172.15, 171.49, 155.89, 155.02, 114.94, 114.87, 114.77, 77.99, 40.01, 39.9-39.08, 38.86, 35.91, 31.3, 28.13. ESI-HR-Mass  $[M+Na]^+ = 538.41$ ,  $[M+K]^+ = 553.38$ ,  $M_{[Calcd]} = 515$ . FT-IR (KBr) 3318, 2979, 2935, 1655, 1520, 1449  $cm^{-1}$ .

### **Immobilization of Boc-YAY-OH on Silica-APS (Sil-YAY)**

Boc-YAY-OH was immobilized onto APS grafted silica (Sil-APS) by covalent linkages using DEPC as coupling reagent. APS-modified silica (3.0 g) was added to a 100 ml three-neck round-bottomed container. Boc-YAY-OH (2.5 g) was dissolved in 30 ml of THF and added into the container. Then DEPC (1.5g, 9.6 mmol) and TEA (1.1 g, 10.6 mmol) were added to the solution and stirred at 60 °C. After being stirred for 1 day the grafted particles were centrifuged and washed with THF, methanol and diethyl ether several times to remove the unreacted lipid molecule and dried in vacuum. The Sil-YAY particles were characterized by elemental analysis, thermogravimetric analysis (TGA), DRIFT-mode FT-IR spectroscopy and Solid State  $C^{13}$  NMR spectroscopy. *Ref. supporting information Analyst, 2012,137, 2553-2555.*

## **(B) Synthesis of Sil-FUF**

### **a) Boc-Phe(1)-OH (1)**

A solution of phenylalanine 8.25 g (50 mmol) in a mixture of dioxan (100 mL), water (50 mL) and 1M NaOH (50 mL) was stirred and cooled in an ice-water bath. Di-tert-butylpyrocarbonate 10.4 g (52 mmol) was added and stirring was continued at room temperature for 6 hrs. Then the solution was concentrated in vacuo to about 15 to 20 mL, cooled in an ice-water bath, covered with a layer of ethyl-acetate (about 100 mL) and acidified with a dilute solution of KHSO<sub>4</sub> to pH 2-3 (Congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The pure material 1 was obtained. Yield = 11.12 g (42 mmol, 84%). (Found: C, 63.12; H, 7.24; N, 5.01%. C<sub>14</sub>H<sub>19</sub>NO<sub>4</sub> (265) requires: C, 63.34; H, 7.17; N, 5.28%).

### **b) Boc-Phe(1)-Aib(2)-OMe (2)**

9.27 g (35 mmol) of Boc-Phe(1)-OH was dissolved in a mixture of 20 mL dichloromethane (DCM) in an ice-water bath. H-Aib-OMe was isolated from 8.2 g (70 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentration to 10 mL and this was added to the reaction mixture, followed immediately by 7.21 g (35 mmol) of di-cyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 24 hrs. DCM was evaporated, residue was taken in ethyl acetate (60 mL), and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2M HCl (3 × 50 mL), brine (2 × 50 mL), 1M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) respectively. Then dried over anhydrous sodium sulfate, and

evaporated in vacuo to yield 2 as a solid sample. Yield = 9.0 g (24.7 mmol, 71%). (Found: C, 62.4; H, 7.32; N, 7.21%.  $C_{19}H_{28}N_2O_5$  (364) requires: C, 62.63 H, 7.69; N, 7.69%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.24-7.19 (ring Hs of Phe, 5H, m); 6.06 (Aib NH, 1H, s); 5.04 (Phe NH, 1H, b); 4.21-4.19 ( $C^\alpha$ H of Phe, 1H, m); 3.71 (-OCH<sub>3</sub>, 3H, s); 3.09-3.04 ( $C^\beta$ H of Aib, 6H, m); 2.99-2.94 ( $C^\beta$ Hs of phe, 2H, m); 1.42 (Boc-CH<sub>3</sub>s, 9H, s).

### c) Boc-Phe(1)-Aib(2)-OH (3)

To 8.0 g (22 mmol) of Boc-Phe(1)-Aib(2)-OMe, 30 mL MeOH and 20 mL of 2M NaOH were added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under vacuo, the residue was taken in 50 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated in vacuo to yield 3 as a solid compound. Yield = 4.62 g (13.2 mmol, 60%). Found: C, 61.51; H, 7.21; N, 9.97%.  $C_{18}H_{26}N_2O_5$  (350) requires C, 61.74, H, 7.42, N, 8.00%.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.22-7.17 (ring Hs of Phe(1), 5H, m); 6.28 (Aib NH, 1H, s); 5.18-5.16 (Phe (1) NH, 1H, d); 4.24-4.17 ( $C^\alpha$ H of Phe(1), 1H, m); 3.07-3.00 ( $C^\beta$ H of Aib, 6H, m); 2.96 ( $C^\beta$ Hs of phe (1), 2H, m); 1.39 (Boc-CH<sub>3</sub>, 9H, s).

### d) Boc-Phe(1)-Aib(2)-Phe(3)-OMe (4)

4.2 g (12 mmol) of Boc-Phe(1)-Aib(2)-OH in 10 mL of DMF was cooled in an ice-water bath and H-Phe-OMe was isolated from 4.3 g (24 mmol) of the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentration to 10

mL and it was added to the reaction mixture, followed immediately by 2.47 g (12 mmol) DCC and 1.62 g (12 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 2M HCl (3 × 50 mL), brine (2 × 50 mL), 1M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) respectively. Then dried over anhydrous sodium sulfate and evaporated in vacuo to yield peptide 4 as yellowish- white solid. Yield = 4.9 g (9.6 mmol, 80%). (Found: C, 65.71; H, 7.11; N, 8.03%.  $C_{28}H_{37}N_3O_6$  (511) requires C, 65.75; H, 7.24; N, 8.21%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.31-7.28 (ring Hs of Phe(3), 5H, m); 7.24-7.19 (ring Hs of Phe(1), 5H, m), 6.79 (Phe(3) NH, 1H, d); 6.06 (Aib NH, 1H, s); 5.04 (Phe NH(1), 1H, b); 4.82-4.77 ( $C^\alpha$ H of Phe(3), 1H, m); 4.21-4.19 ( $C^\alpha$ H of Phe(1), 1H, m); 3.71 (-OCH<sub>3</sub>, 3H, s); 3.17-3.12 ( $C^\beta$ Hs of Phe(3), 2H, m); 3.09-3.04 ( $C^\beta$ H of Aib, 6H, m); 2.99-2.94 ( $C^\beta$ Hs of phe (1), 2H, m); 1.42 (Boc-CH<sub>3</sub>s, 9H, s). FT-IR (KBr): 3436, 3417, 3279, 2979, 2932, 1744, 1709, 1692, 1665, 1521, 1495, 1445, 1365, 1284, 1173  $cm^{-1}$ .

#### e) Boc-Phe(1)-Aib(2)-Phe(3)-OH (5)

To 4.6 g (9 mmol) of Boc-Phe(1)-Aib(2)-Phe(3)-OMe, 30 mL MeOH and 20 mL of 2M NaOH were added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under vacuo, the residue was taken in 50 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts were pooled, dried over anhydrous sodium sulfate, and evaporated in vacuo to yield 5 as a solid compound. Yield = 3.0 g (6 mmol, 65%). Found: C, 52.1; H, 7.1; N, 10.2%.  $C_{27}H_{35}N_3O_6$  (497) requires C, 65.19, H, 7.04, N, 8.45%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 7.30-7.26 (ring Hs of

Phe (3), 5H, m ); 7.22-7.17 (ring Hs of Phe (1), 5H, m); 6.91-6.89 (Phe (3) NH, 1H, d); 6.28 (Aib NH, 1H, s); 5.18-5.16 (Phe (1) NH, 1H, d); 4.73-4.71 (C<sup>α</sup>H of Phe (3), 1H, m); 4.24-4.17 (C<sup>α</sup>H of Phe (1), 1H, m); 3.30-3.25 (C<sup>β</sup>Hs of Phe (3), 2H, m); 3.07-3.00 (C<sup>β</sup>H of Aib, 6H, m); 2.96 (C<sup>β</sup>Hs of phe (1), 2H, m); 1.39 (Boc-CH<sub>3</sub>, 9H, s). FT-IR (KBr) : 3411, 3312, 2981, 2936, 1686, 1662, 1519, 1455, 1391, 1368, 1289, 1174 cm<sup>-1</sup>. EI-MS m/Z: [M+ Na]<sup>+</sup> = 519.9763, [M+ K]<sup>+</sup> = 536.6430, M<sub>calcd</sub> = 497.

### **Immobilization of Boc-FUF-OH molecule over silica surface (Sil-FUF)**

Boc-FUF-OH was immobilized onto APS grafted silica (Sil-APS) by covalent linkages using DEPC. APS-modified silica (3.0 g) was added to a 100 ml three-neck round-bottomed container. Sil-APS (3.0 g) and FUF (2 .0 g) were taken in 30 ml THF and stirred. Then DEPC (1.5g, 9.6 mmol) and TEA (1.1 g, 10.6 mmol) were added to the solution and stirred at 60 °C. After being stirred for 1 day the grafted particles were centrifuged and washed with THF, methanol and diethyl ether several times to remove the unreacted lipid molecule and dried in vacuum. *Ref. Journal of Chromatography A*, **2012**, 1226, 43-52.

### **(C) Synthesis of Sil-Lysine-Fmoc**

#### **a). Synthesis of Fmoc-Lysine**

20 mmol (2.92 g) of Lysine was dissolved in a basic sodium carbonate solution (150 mL). It was cooled in an ice-water bath and a cooled solution of 40 mmol Fmoc-Cl (10.26 g) in dioxane (150 mL) was added to it. The reaction mixture was allowed to come to room temperature and stirred for 24 h. Then the solution was concentrated in vacuum to about 15 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 100 mL), and acidified with a dilute HCl to

neutral pH. The aqueous phase was extracted with ethyl acetate and this operation was done twice. The ethyl acetate extract was pooled, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuum. A transparent solid material was obtained and this was characterized by FT-IR spectrometry,  $^1\text{H-NMR}$  spectroscopy. Yield = 8.0 g (14.44 mmol, 72%). (Found: C, 71.41; H, 6.11; N, 5.03%.  $\text{C}_{33}\text{H}_{34}\text{N}_2\text{O}_6$  (554) requires C, 71.48; H, 6.13; N, 5.05%.)

**$^1\text{H-NMR}$  spectra of Fmoc-(L)Lys.** (400 MHz,  $\text{CDCl}_3$ , 25° C): 7.78- 7.69 (m, 2H; aromatic CH),  $\delta$  7.74- 7.72 (d, 1H, NH (1),  $J=8\text{Hz}$ ),  $\delta$  7.63- 7.61 (d, 2H; aromatic CH,  $J= 8\text{Hz}$ ),  $\delta$  7.56 (d, 1H, NH (2),) 7.4- 7.31 (m, 2H; aromatic CH),  $\delta$  4.4-4.38 (m, 3H; CH and CH<sub>2</sub>),  $\delta$  4.13-4.1 (m, 1H;  $\alpha$  CH),  $\delta$  3.14(m, 2H;  $\delta$  CH<sub>2</sub>), 1.8 (m, 2H;  $\gamma$  CH<sub>2</sub>),  $\delta$  1.4 (m, 2H;  $\beta$  CH<sub>2</sub>).

**FT-IR (KBr):** 3325, 3064, 2947, 1692, 1535, 1449, 1340, 1255 $\text{cm}^{-1}$ .

### **Immobilization of Fmoc-Lysine molecule over silica surface (Sil-Ly-Fmoc)**

Sil-APS (3.0 g) and Fmoc-lysine (3.0 g) were taken in 30 ml THF and stirred. Then DEPC (1.5g, 9.6 mmol) and TEA (1.1 g, 10.6 mmol) were added to the solution and stirred at 60 C. After being stirred for 1 day the grafted particles were centrifuged and washed with THF, methanol and diethyl ether several times to remove the unreacted molecule and dried in vacuum.

### **(D) Synthesis of Sil-DYS**

#### **a) Preparation of Stearyl <sup>D</sup>Tyrosinamide (SDY)**

##### **1. N-Stearyl-<sup>D</sup>-tyrosinamide-methyl ester (1)**

4.3 g (15 mmol) of stearic acid was taken in 10 mL of DMF was cooled in an ice-water bath and H-<sup>D</sup>Tyr-OMe was isolated from 5.85 g (30 mmol) of the corresponding methyl ester

hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentration to 10 mL and it was added to the reaction mixture, followed immediately by 3.09 g (15 mmol) DCC and 2.2 g (15 mmol) of HOBt. The reaction mixture was stirred for two days. The residue was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 2M HCl (3 × 50 mL), brine (2 × 50 mL), 1M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) respectively. Then dried over anhydrous sodium sulfate and evaporated in vacuo to yield 1 as a white solid.

Yield = 5.6 g (12.1 mmol, 80%). C<sub>28</sub>H<sub>47</sub>NO<sub>4</sub> (461) requires C, 72.88; H, 10.1; N, 3%. Found C, 72.62; H, 9.91; N, 2.97% <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.25-8.23 (Tyr NH, 1H, d, J = 8Hz); 6.98-6.96 (ring Hs of Tyr, 2H, d, J = 8Hz); 6.67-6.65 (ring Hs of Tyr, 2H, d, J = 8Hz); 4.34 (C<sup>α</sup>H of Tyr, 1H, m); 3.57 (-OCH<sub>3</sub>, 3H, s); 2.89-2.76 (C<sup>β</sup>Hs of Tyr, 2H, dd); 2.06-2.02 (-CO-CH<sub>2</sub>, 2H, t); 1.64 (-CO-C-CH<sub>2</sub>-, 2H, b); 1.39 (-(CH<sub>2</sub>)<sub>14</sub>-, 28 H, b); 0.85-0.83 (-CH<sub>3</sub>, 3H, t). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 172.38, 171.85, 130.1, 127.33, 53.80, 51.62, 40.12, 39.7-38.87, 35.39, 33.54, 31.24, 29.00, 28.88-28.44, 25.11, 22.05, 13.92. FT-IR data: ν<sub>max</sub> (KBr) / cm<sup>-1</sup> 3332, 2917, 2849, 1752, 1648, 1558, 1463, 1229, 1165. ESI-HR-Mass [M+H]<sup>+</sup> = 462.28, [M+Na]<sup>+</sup> = 484.12, [M+K]<sup>+</sup> = 500.05, M<sub>calcd</sub> = 461.

## 2. N-Stearyl-D-tyrosinamide (SDY) (2)

To 5.4 g (11.7 mmol) of 1, 20 mL MeOH and 10 mL of 2M NaOH were added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under vacuo, the residue was taken in 50 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts

were pooled, dried over anhydrous sodium sulfate, and evaporated in vacuo to yield 2 as a solid compound.

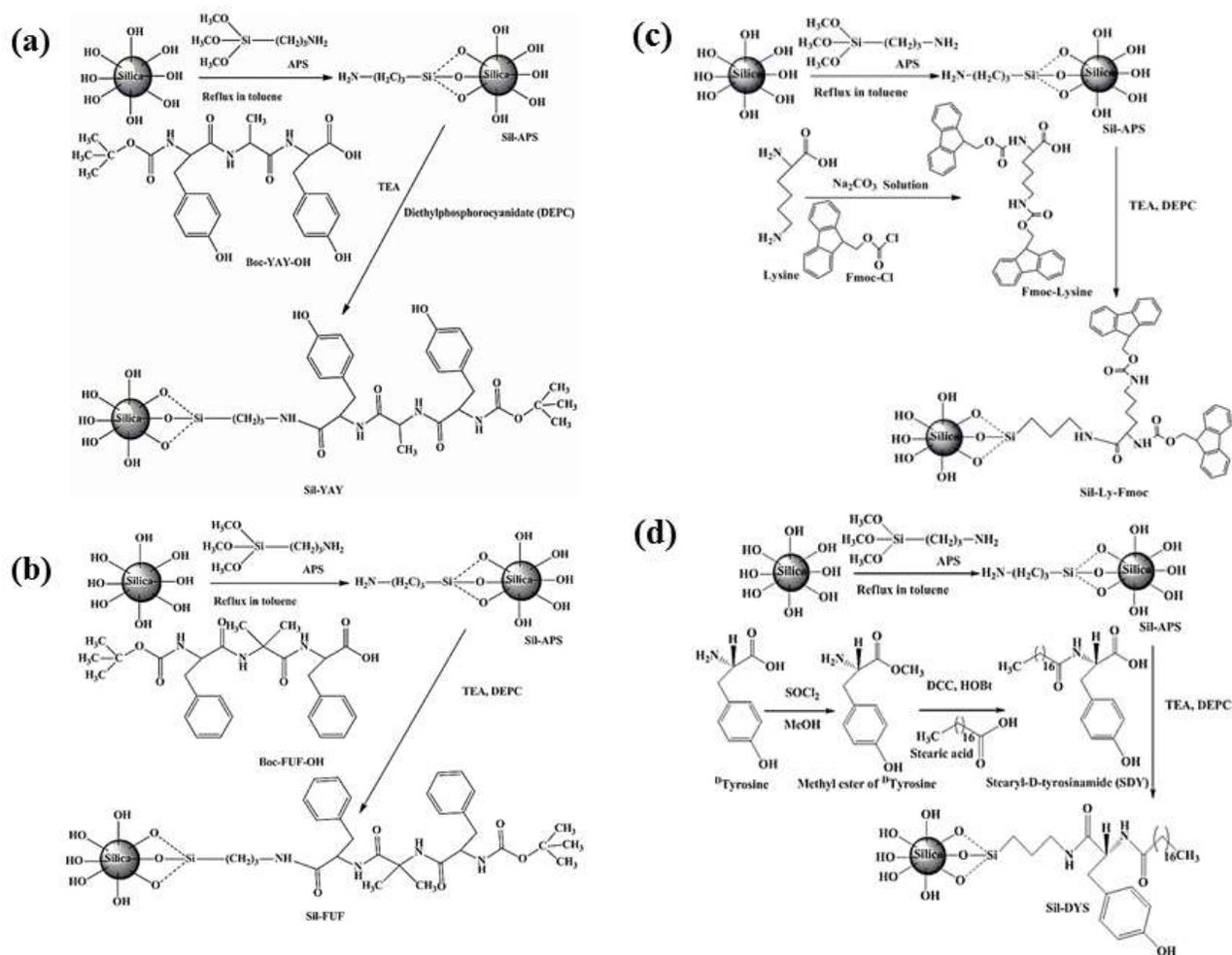
Yield = 2.3 g (5.14 mmol, 44%).  $C_{27}H_{45}NO_4$  (447) requires C, 72.48, H, 10.06, N, 3.13%. Found C, 72.28, H, 9.87, N, 2.98%. M. p 129-130 °C.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.21 (Ph-OH, 1H, b) 8.02-8.00 (Tyr NH, 1H, d, J = 8Hz); 7.00-6.98 (ring Hs of Tyr, 2H, d, J = 8Hz); 6.64-6.62 (ring Hs of Tyr, 2H, d, J = 8Hz); 4.32-4.31 ( $C^\alpha$ H of Tyr, 1H, m); 2.92-2.88 ( $C^\beta$ Hs of Tyr, 2H, dd); 2.19-2.15 (-CO-CH $_2$ -, 2H, t); 1.40-1.36 (-CO-C-CH $_2$ -, 2H, b); 1.23 (-(CH $_2$ ) $_{14}$ -, 28 H, b); 0.86-0.83 (-CH $_3$ , 3H, t).  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  174.43, 173.31, 172.09, 155.86, 129.90, 127.68, 114.86, 53.61, 40.12, 39.91-38.87, 35.99, 35.0, 33.64, 31.27, 29.02-28.49, 25.17, 24.47, 22.07, 13.92. FT-IR data:  $\nu_{max}$  (KBr) /  $cm^{-1}$  3313, 3240, 2917, 2849, 1708, 1645, 1542, 1516, 1462, 1235. ESI-HR-Mass  $[M+H]^+ = 447.41$ ,  $[M+Na]^+ = 470.27$ ,  $[M+K]^+ = 486.43$ ,  $M_{calcd} = 447$ .

### **Immobilization of SDY on to silica surface (Sil-DYS)**

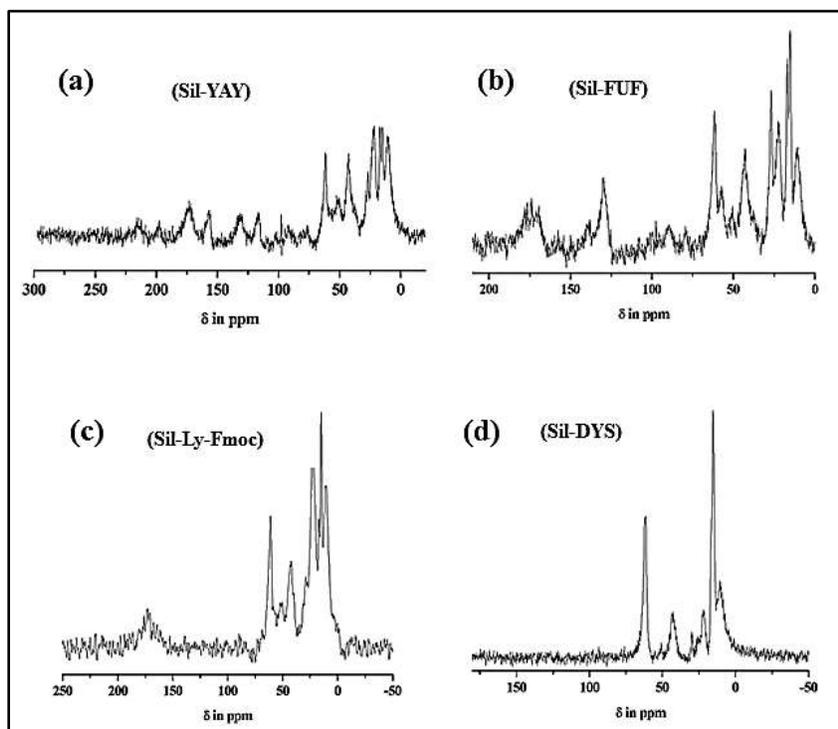
Silica-APS (3.0 g) and SDY (3.0 g) were taken in 100 ml dry THF and stirred. DEPC (1.5 g) and TEA (1.1 g) were added to the solution and stirred at 60 °C. After being stirred for 1 day the grafted particles (Sil-DYS) were washed with chloroform and methanol several times to remove the unreacted lipid molecule and dried in vacuum. *Ref.* supporting information *Nanotechnology*, **2012**, *23*, 495301.

### Elemental analysis

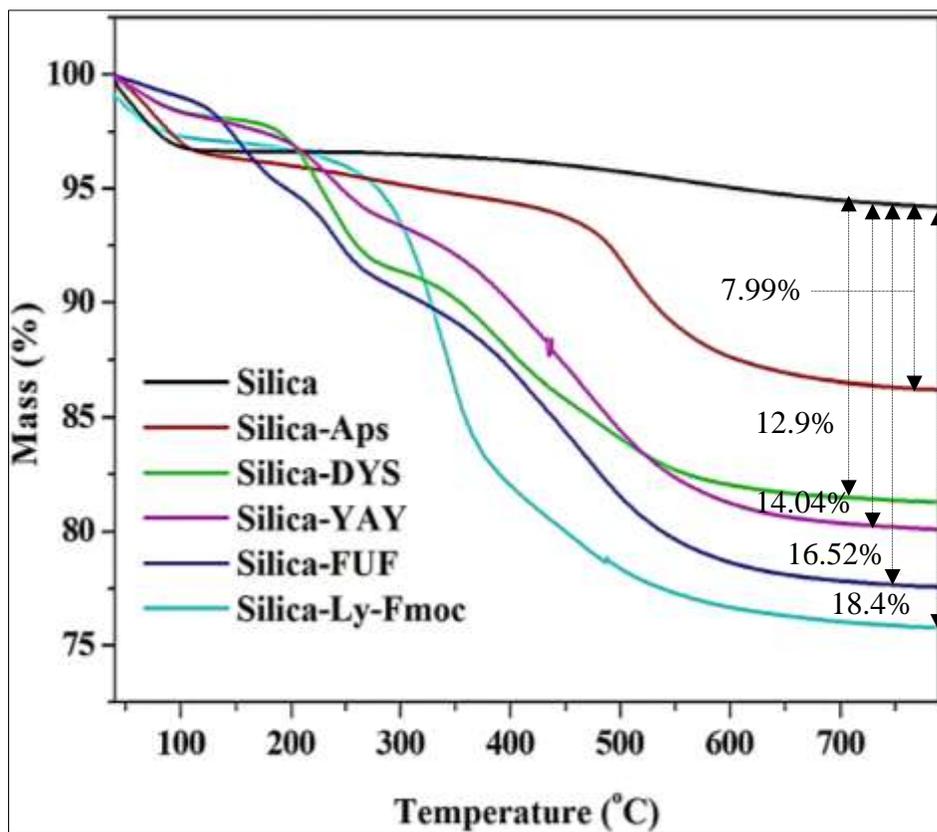
<b>Sample</b>	<b>%C (wt %)</b>	<b>%H (wt %)</b>	<b>%N (wt %)</b>	<b>C/N</b>	<b>Grafted amounts (wt %) from TGA</b>
<b>Sil-APS</b>	7.1	2.0	2.4	2.95	7.99
<b>Sil-YAY</b>	13.37	2.75	2.80	4.77	14.04
<b>Sil-FUF</b>	12.32	2.77	2.31	5.33	16.52
<b>Sil-Ly-Fmoc</b>	14.34	2.81	3.03	4.73	18.39
<b>Sil-DYS</b>	9.1	2.62	1.78	5.11	12.9



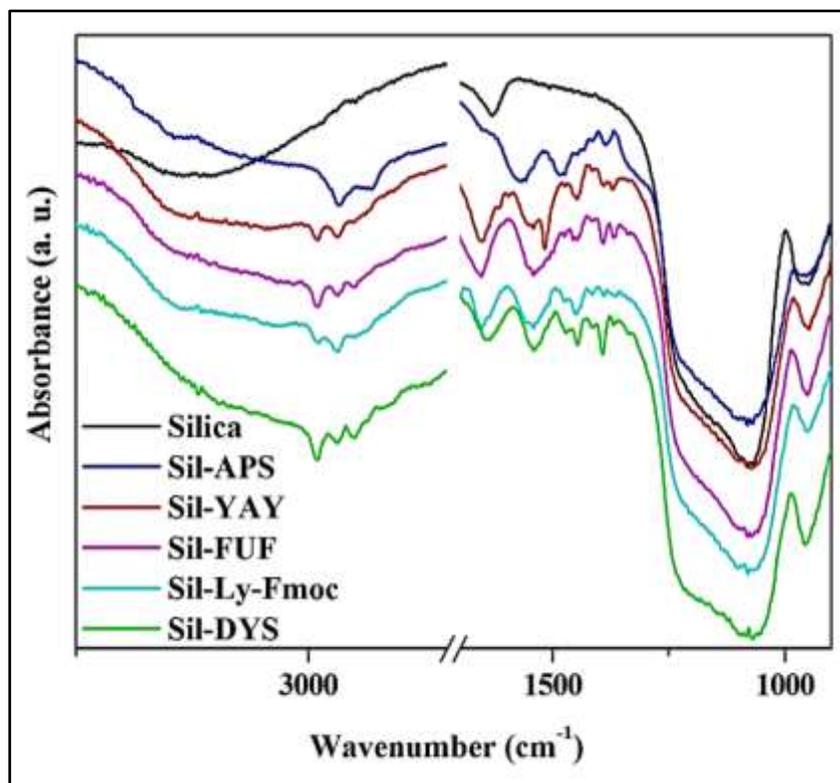
**Fig. S1** Synthetic scheme showing the routes for synthesizing (a) Sil-YAY, (b) Sil-FUF, (c) Sil-Ly-Fmoc and (d) Sil-DYS.



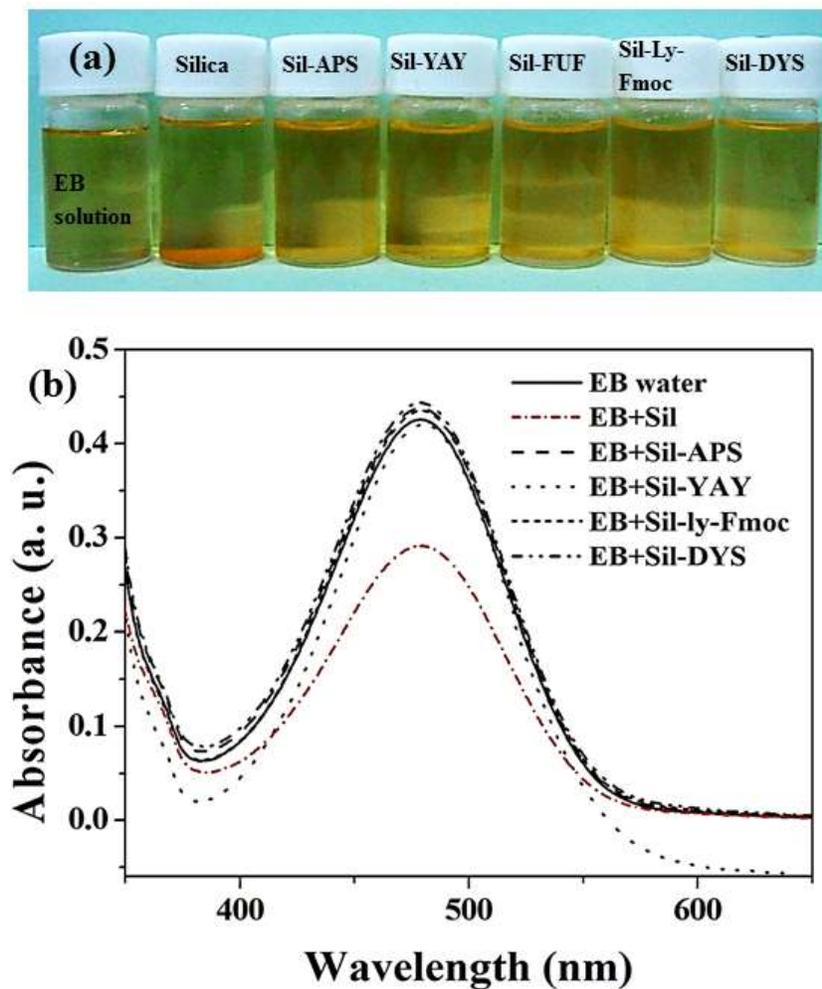
**Fig. S2** Solid State  $^{13}\text{C}$  NMR spectra of surface modified silica particles.



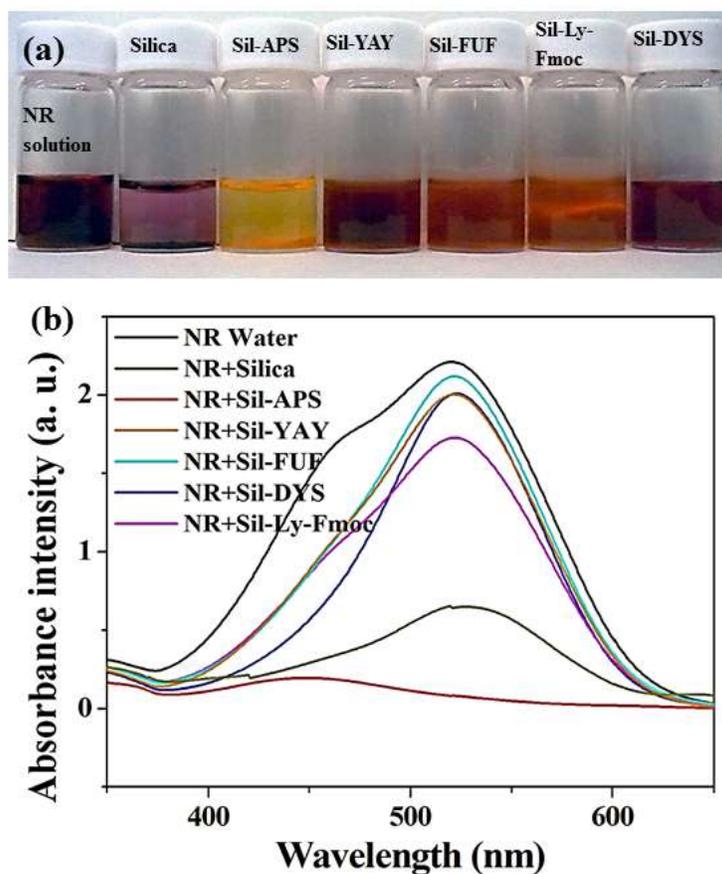
**Fig. S3** Thermogravimetric data (TGA) of bare silica particles and surface modified silica particles.



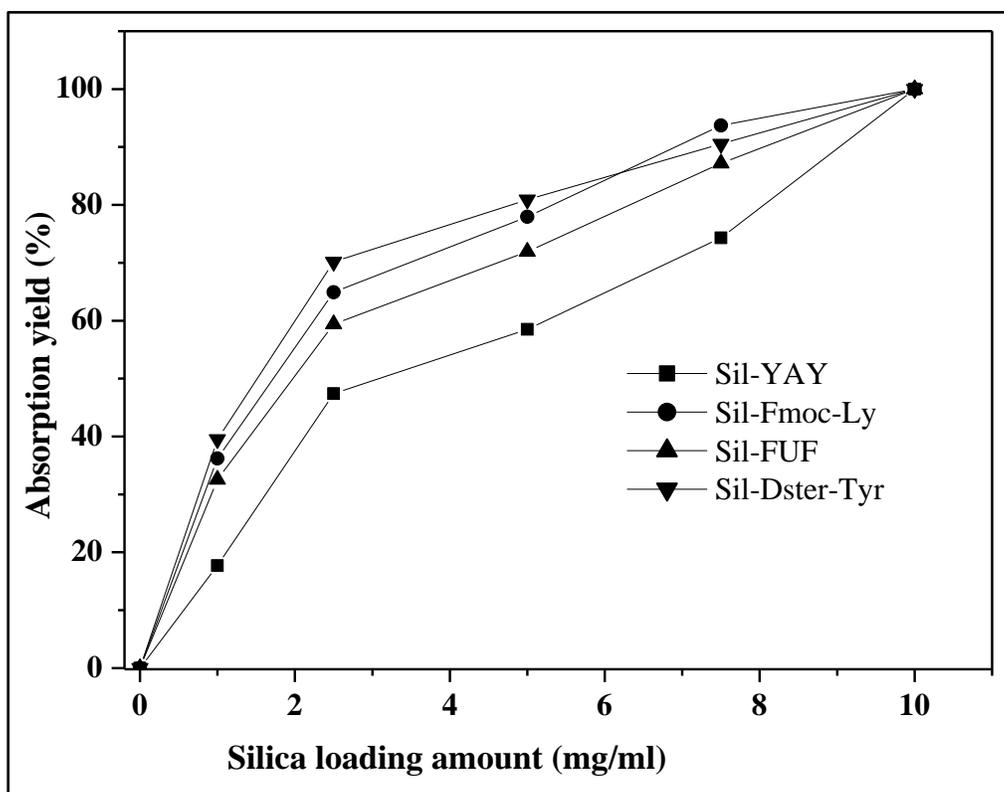
**Fig. S4** DRIFT-mode FT-IR spectra of bare silica particles and surface modified silica particles.



**Fig. S5** (a) Photographs of aqueous solutions of cationic Ethidium bromide (EB) dye after overnight adsorption with organically modified silica particles respectively and (b) UV-Vis absorption spectra of EB dye after adsorption examination with organically modified silica particles.



**Fig. S6** (a) Photographs of aqueous solutions of Neutral Red (NR) dye after overnight adsorption with organically modified silica particles respectively and (b) UV-Vis absorption spectra of NR dye after adsorption examination with organically modified silica particles.



**Fig. S7** Plot of adsorption yield of Methyl Orange (MO) dye versus quantity of surface modified silica particles.