Supporting information

Preparation of Hyperstar Polymers with Encapsulated Au$_{25}$(SR)$_{18}$ Clusters

as Recyclable Catalysts for Nitrophenol Reduction

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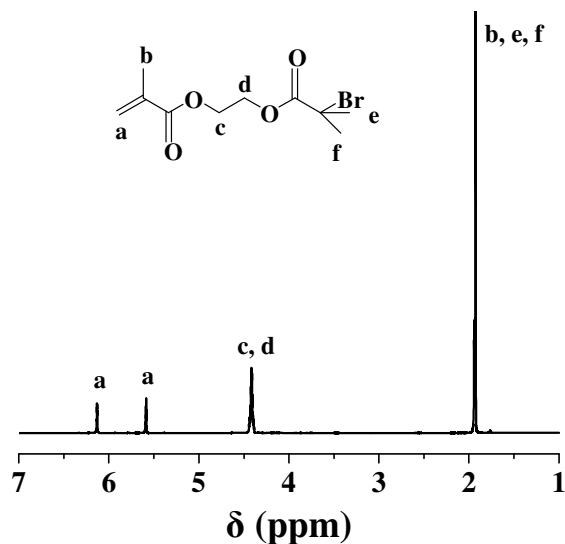
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Figure S1. ^{1}H NMR spectrum of inimer BIEM. NMR condition: 25 °C, CDCl$_3$ as
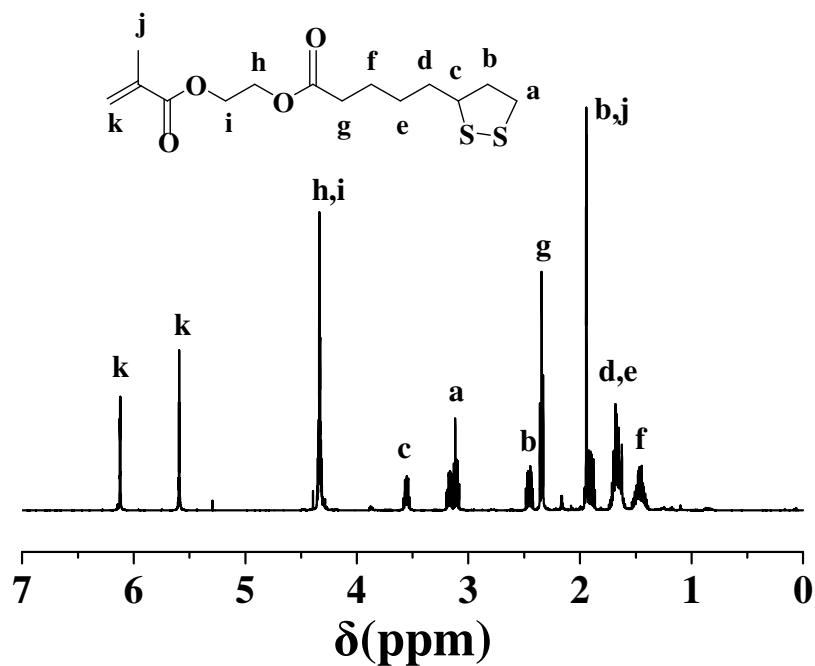
solvent.

Figure S2. ^{1}H NMR spectrum of monomer MAOELP. NMR condition: 25 ^{o}C, CDCl$_3$ as solvent.
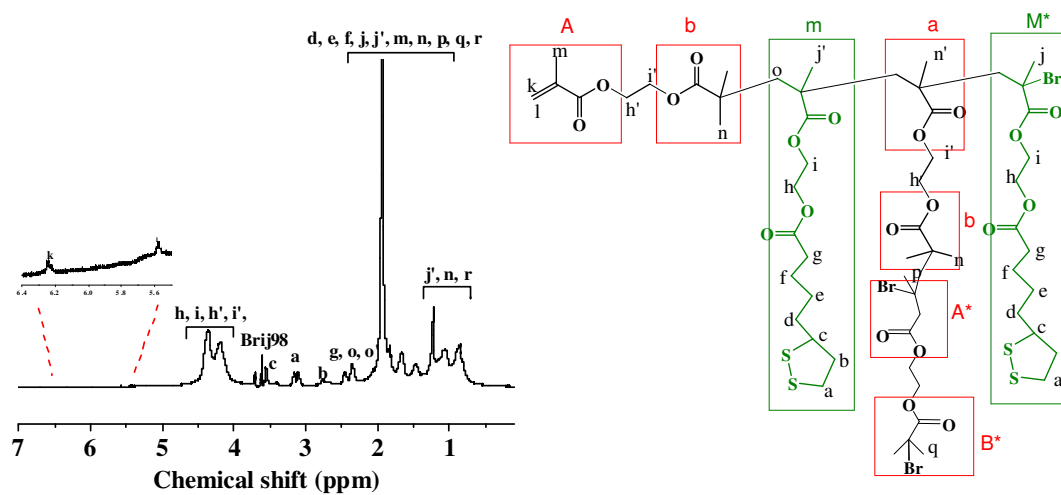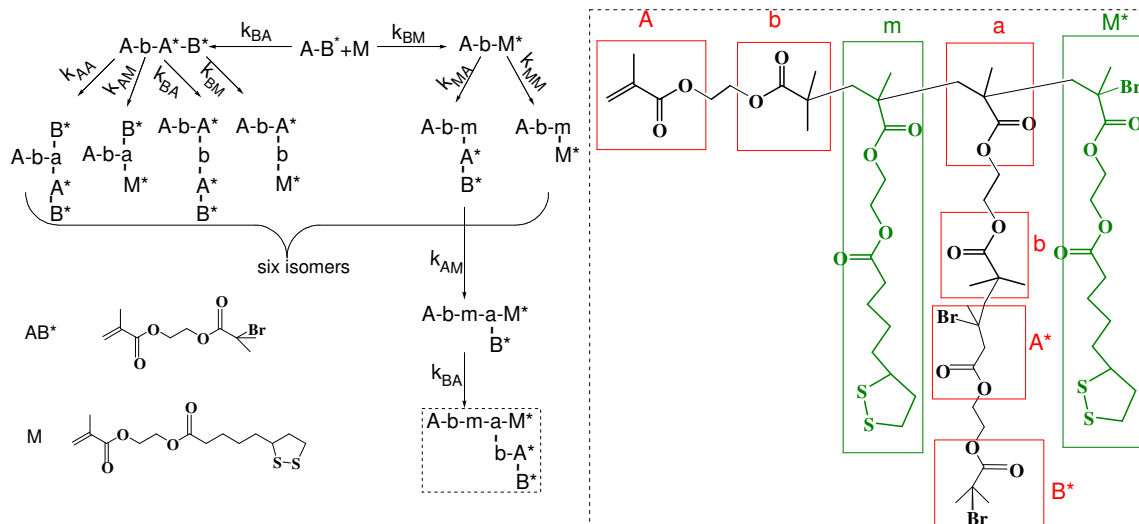

Figure S3. ^{1}H NMR spectrum of HB-(MAOELP$_1$-*r*-BIEM$_5$). NMR condition: 25 ^{o}C, CDCl$_3$ as solvent.

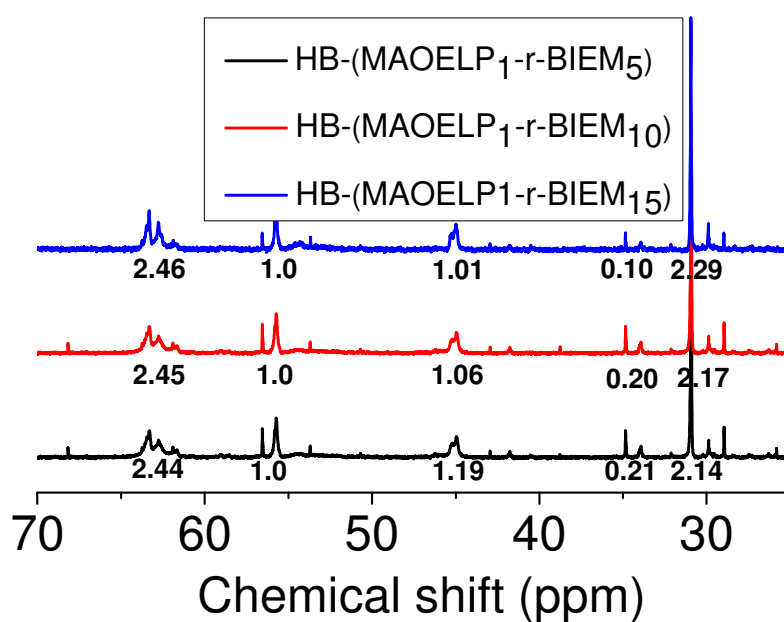**Scheme S1.** Illustration of the mechanism for copolymerization of inimer BIEM with monomer MAOELP.

Figure S4. Inverse-gated decoupled spectra of the hyperbranched copolymer HB-(MAOELP$_1$-r-BIEM$_5$), HB-(MAOELP$_1$-r-BIEM$_{10}$) and HB-(MAOELP$_1$-r-BIEM1$_5$) synthesized via copolymerization of BIEM and MAOELP in microemulsion.

Detailed calculation of the degree of branching (DB) of hyperbranched

copolymers.

Since the conversion of methacrylate group in BIEM and MAOELP was > 99%, determined by ^{1}H NMR, a full conversion of methacrylate groups (conv.$_A$ = 1, conv.$_M$ = 1) was applied to simplify the calculation. Based on the spectra in Figure S3:

1. Hyperbranched polymer HB-(MAOELP$_1$-r-BIEM$_5$)

$N_b = N_{A*} + N_{M*} = 0.14$

$N_{B*} = N_a + N_A - N_{M*} = 1.0$

$f_{B*} = N_{B*}/(N_{B*} + N_b) = 1/1.14 = 0.88$

$r = k_{A*}/k_{B*} = (con\ v._A + f_{B*} - 1)/(-\ln f_{B*} + f_{B*} - 1) = 112$

DB' = 0.21

Actual DB = 0.21×(5/6) = 0.18

2. Hyperbranched polymer HB-(MAOELP$_1$-r-BIEM$_{10}$)

$N_b = N_{A*} + N_{M*} = 0.17$

$N_{B*} = N_a + N_A - N_{M*} = 1.0$

$f_{B*} = N_{B*}/(N_{B*} + N_b) = 1/1.17 = 0.85$

$r = k_{A*}/k_{B*} = (con\ v._A + f_{B*} - 1)/(-\ln f_{B*} + f_{B*} - 1) = 0.85/0.0125 = 68$

DB' = 0.25

Actual DB = 0.25× (10/11) = 0.23

3. Hyperbranched polymer HB-(MAOELP$_1$-r-BIEM$_{15}$)

$N_b = N_{A*} + N_{M*} = 0.29$

$N_{B*} = N_a + N_A - N_{M*} = 1.0$

$f_{B*} = N_{B*}/(N_{B*} + N_b) = 1/1.29 \approx 0.78$

$r = k_{A*}/ k_{B*} = (\text{con } v._A + f_{B*} -1)/(-\ln f_{B*} + f_{B*}-1)=0.78/0.0125=28$

DB' = 0.34

Actual DB = 0.34×(15/16) = 0.32

Table S1. DBs of different hyperbranched copolymers

Polymer	DB
HB-(MAOELP$_1$-r-BIEM$_5$)	0.18
HB-(MAOELP$_1$-r-BIEM$_{10}$)	0.23
HB-(MAOELP$_1$-r-BIEM$_{15}$)	0.32
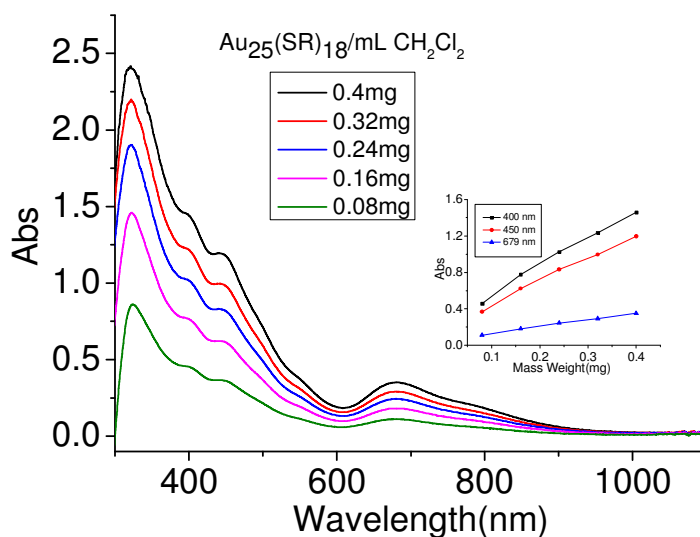
Figure S5. UV-Vis absorption spectra of Au$_{25}$(SR)$_{18}$ in CH$_2$Cl$_2$ at various concentrations with calibration curves as inset.
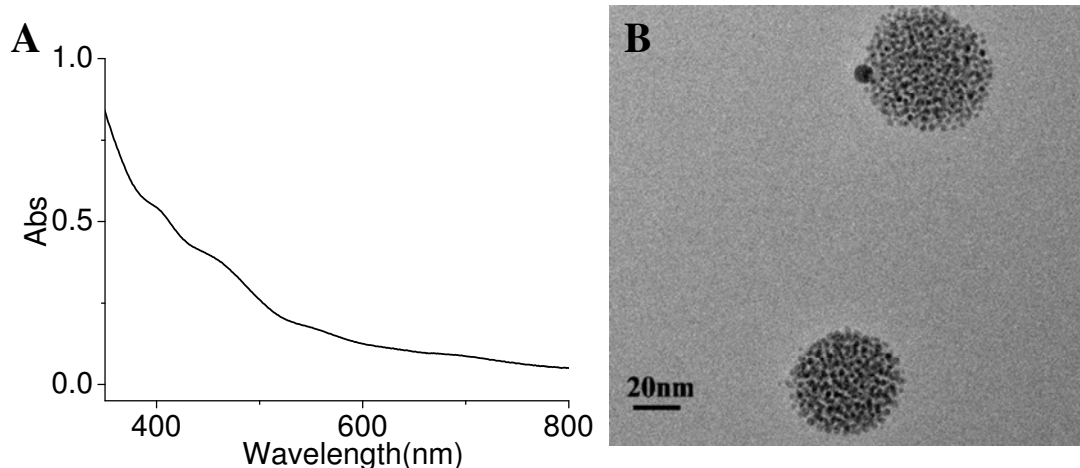
Figure S6. (A) UV-Vis absorption spectrum and (B) TEM image of HS-Au$_{25}$(SR)$_{18}$ nanocomposites after storage in 3 months.

Catalytic reduction reaction of 4-nitrophenol

The ratio of absorbance A_t of 4-nitrophenolate at time t to its value A_0 at t=0 (A_t/A_0) could be directly interpreted as the ratio of the respective concentrations C_t/C_0. Therefore, the reaction conversion at time t can be calculated according to equation (1):

Conversion (%) = (1- C_t/C_0) × 100 = (1 -A_t/A_0) × 100 (1)

The concentration of sodium borohydride was set to be 50 times higher than that of 4-nitrophenol and therefore was assumed as a constant during the reaction. Accordingly, the catalytic rate was evaluated through pseudo-first-order kinetics with respect to 4-nitrophenol, being independent of NaBH$_4$ concentration. The calculation equation was as follows:

dC_t/dt = -$k_{app}t$ or ln(C_t/C_0) = ln(A_t/A_0) = -$k_{app}t$ →

ln(A_0/A_t) = $k_{app}t$ (2)

Figure S7. Digital pictures during 4-nitrophenol reduction reaction.

Table S2. Catalytic results of 4-nitrophenol reduction reaction

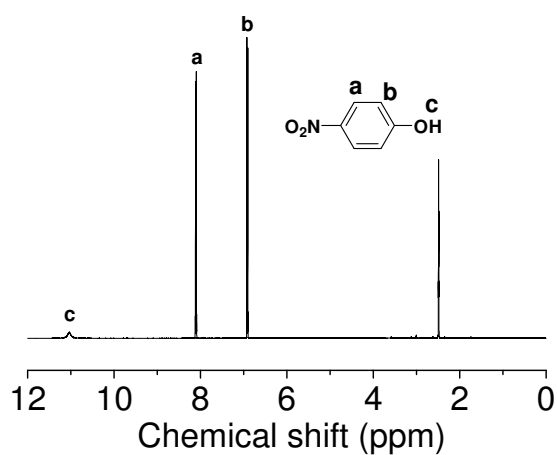| Catalyst	K_{app} (min^{-1})	Conv. 4-nitrophenol (%)	Yield 4-aminophenol (%)
Au$_{25}$(SR)$_{18}$	0.140±0.013	100	98
1st cycle HS-Au$_{25}$(SR)$_{18}$	0.129±0.007	100	96
2nd cycle HS-Au$_{25}$(SR)$_{18}$	0.124±0.017	100	95
3rd cycle HS-Au$_{25}$(SR)$_{18}$	0.119±0.009	100	96
4th cycle HS-Au$_{25}$(SR)$_{18}$	0.118±0.004	100	95
5th cycle HS-Au$_{25}$(SR)$_{18}$	0.108±0.004	100	95

Figure S8. ^{1}H NMR spectrum of 4-nitrophenol. NMR condition: 25°C, DMSO-d_6 as solvent.
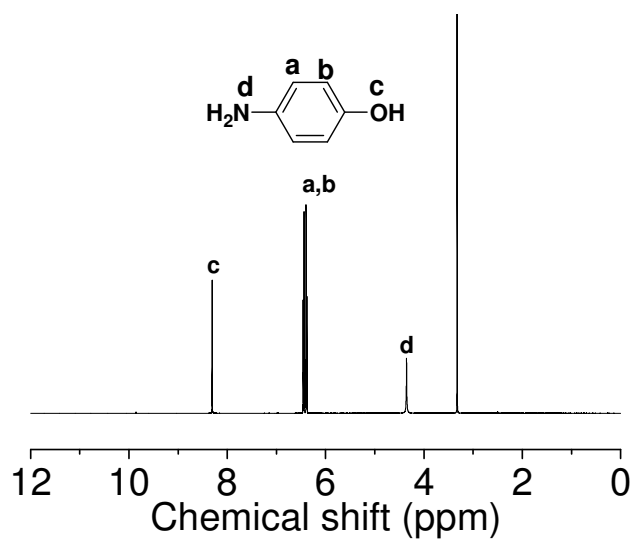
Figure S9. ^{1}H NMR spectrum of 4-aminophenol. NMR condition: 25°C, DMSO-d_6 as solvent.