Social Self-Sorting in Aqueous Solution – Supporting Information

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Synthetic Procedures and Characterization.

General. Starting materials were purchased from commercial suppliers and were used without further purification. Compound **SI1** was prepared according to the literature procedure.¹ Melting points were measured in open capillary tubes and are uncorrected. NMR spectra were measured on spectrometers operating at 400 or 500 MHz for ¹H and 100 or 125 MHz for ¹³C. Mass spectrometry was performed using a magnetic sector instrument by electron impact (EI) or by fast atom bombardment (FAB) using the indicated matrix. The matrix “magic bullet” is a 5:1 (w:w) mixture of dithiothreitol:dithioerythritol. Electrospray mass spectrometry (ES-MS) experiments were performed on an ion-trap mass spectrometer equipped with a nanospray source.

Compound 2. A mixture of **SI1** (159 mg, 0.17 mmol) and LiOH (42 mg, 1.75 mmol) was suspended in a mixture of MeOH (45 mL) and water (45 mL). The resulting suspension was heated at 70 °C for 45 h. The reaction mixture was concentrated, dissolved in a minimum amount of H₂O, and neutralized with HClO₄ (180 μL, 2.09 mmol). The suspension was centrifuged, the supernatant pipetted off, and the residue was washed with water. An aq. solution of the product was lyophilized to yield **2** as a fluffy solid (110 mg, 0.14 mmol, 79%). M.p. > 285 °C (dec.). IR (KBr, cm⁻¹): 1734s, 1465m, 1283w, 912m, 766w. ¹H NMR (400 MHz, DMSO-*d*₆): 7.34 (br. m, 4H), 7.26 (br. m, 4H), 5.69 (d, *J* = 15.7, 2H), 4.96 (d, *J* = 15.7, 2H), 4.79 (d, *J* = 16.1, 4H), 4.64 (d, *J* = 16.1, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆): 166.5, 165.7, 154.8, 150.8, 138.3, 128.8, 127.2, 79.5, 79.3, 47.8, 46.0. ES-MS: *m/z* 793 (100, [M + H]⁺). HR-MS (ES): *m/z* 793.1726 ([M + H]⁺, C₃₄H₂₅N₁₂O₁₂, calcd 793.1715).

References:

(1) Wu, A.; Chakraborty, A.; Witt, D.; Lagona, J.; Damkaci, F.; Ofori, M. A.; Chiles, J. K.; Fettingner, J. C.; Isaacs, L. *J. Org. Chem.* **2002**, 67, 5817-5830.

Models Used for the Simulations Reported in Figures 3 and 4.

Model for Figure 3.

```
clear all
```

```
% Lines start with % are just comments
```

```
% These are the known quantities
```

```
Kam = 3000000;
```

```
Kan = 100000;
```

```
Kbm = 100000;
```

```
Kbn = 3000000;
```

```
At = 0.001;
```

```
Bt = 0.001;
```

```
% This sets up the independent variable
```

```
MMt = logspace(-6, -4, 100)
```

```
ln = length(MMt)
```

```
for im = 1:ln
```

```
    Mt = MMt(im);
```

```
    Nt = MMt(im);
```

```
% Make the unknown variables symbolic
```

```
syms AM BM AN BN A B M N real
```

```
% These are equations
```

```
s1 = Kam*A*M - AM;
```

```
s2 = Kan*A*N - AN;
```

```
s3 = Kbm*B*M - BM;
```

```
s4 = Kbn*B*N - BN;
```

```
s5 = A + AM + AN - At;
```

```
s6 = B + BM + BN - Bt;
```

```
s7 = M + AM + BM - Mt;
```

```
s8 = N + AN + BN - Nt;
```

```
% Find numerical solutions
```

```
S = solve(s1, s2, s3, s4, s5, s6, s7, s8, 'A,B,M,N,AM,BM,AN,BN');
```

```
% pick up only the real solution
```

```
for i = 1:6 % for 6 solutions
```

```
    if (double(S.A(i)) >= 0 & ...
```

```
        double(S.B(i)) >= 0 & ...
```

```
        double(S.M(i)) >= 0 & ...
```

```
        double(S.N(i)) >= 0 & ...
```

```
        double(S.AM(i)) >= 0 & ...
```

```
        double(S.AN(i)) >= 0 & ...
```

```

        double(S.BM(i)) >= 0 & ...
        double(S.BN(i)) >= 0)
        Aans=double(S.A(i));
        Bans=double(S.B(i));
        Mans=double(S.M(i));
        Nans=double(S.N(i));
        AMans=double(S.AM(i));
        BMans=double(S.BM(i));
        ANans=double(S.AN(i));
        BNans=double(S.BN(i));
    end
end
disp(sprintf(' %10.12f', Mt, Nt, Aans, Bans, Mans, Nans, AMans, BMans, ANans, BNans))

end

```

Model for Figure 4.

clear all

% Lines start with % are just comments

% These are the known quantities

Kam =1000000000;

Kan =10000;

Kbm =1000000;

Kbn =100000;

At =0.001;

Bt =0.001;

%This sets up the independent variable

MMt=logspace(-6,-4,100)

ln=length(MMt)

for im=1:ln

Mt =MMt(im);

Nt =MMt(im);

% Make the unknown variables symbolic

syms AM BM AN BN A B M N real

% These are equations

s1= Kam*A*M - AM;

s2= Kan*A*N - AN;

s3= Kbm*B*M - BM;

s4= Kbn*B*N - BN;

s5= A + AM + AN - At;

s6= B + BM + BN - Bt;

```

s7= M + AM + BM - Mt;
s8= N + AN + BN - Nt;

% Find numerical solutions
S=solve(s1, s2, s3, s4, s5, s6, s7, s8, 'A,B,M,N,AM,BM,AN,BN');

% pick up only the real solution
for i=1:6 % for 6 solutions
    if (double(S.A(i)) >= 0 & ...
        double(S.B(i)) >= 0 & ...
        double(S.M(i)) >= 0 & ...
        double(S.N(i)) >= 0 & ...
        double(S.AM(i)) >= 0 & ...
        double(S.AN(i)) >= 0 & ...
        double(S.BM(i)) >= 0 & ...
        double(S.BN(i)) >= 0)
        Aans=double(S.A(i));
        Bans=double(S.B(i));
        Mans=double(S.M(i));
        Nans=double(S.N(i));
        AMans=double(S.AM(i));
        BMans=double(S.BM(i));
        ANans=double(S.AN(i));
        BNans=double(S.BN(i));
    end
end

disp(sprintf(' %10.12f', Mt, Nt, Aans, Bans, Mans, Nans, AMans, BMans, ANans, BNans))

end

```

Figure S1.1. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 291 K, 1 mM) recorded for an equimolar mixture of: A) **3**, B) **3** and **7**, C) **3** and **1**, D) **3** and **2**, E) **3** and **9**, and F) **3** and **8**.

Figure S1.2. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 291 K, 1 mM) recorded for an equimolar mixture of: A) **4**, B) **4** and **1**, C) **4** and **7**, D) **4** and **6**, E) **4** and **2₂**, and f) **4** and **9₂•10₂**.

Figure S1.3. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 291 K, 1 mM) recorded for an equimolar mixture of: A) **5**, B) **5** and **7**, C) **5** and **1**, D) **5** and **2₂**, E) **5** and **9₂•10₂**, and f) **5** and **6**.

Figure S1.4. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 291 K, 1 mM) recorded for an equimolar mixture of: A) **11**, B) **11** and **7**, C) **11** and **1**, D) **11** and **6**, E) **11** and **2**, and f) **11** and **9₂•10₂**.

Figure S2.1. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 1 mM) recorded for a 10-component equimolar mixture comprising **1** – **8**, **11**, and KCl at: A) 280 K, B) 291 K, C) 308 K, D) 328 K, E) 338 K, and F) upon returning to 291 K.

Figure S2.2. ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 1 mM) recorded for a 9-component equimolar mixture comprising **1**, **3** – **8**, **11**, and KCl at: A) 280 K, B) 291 K, C) 328 K, D) 338 K, E) upon returning to 291 K.

Figure S3. Variable pD ^1H NMR spectra (500 MHz, D_2O , 1 mM) recorded for a mixture of **1** – **11**, and KCl at: A) pD 10.4, B) pD 9.4, C) pD 7.4, D) pD 6.2, E) pD 4.6, F) pD 3.4.

Figure S4. Variable concentration ^1H NMR spectra (500 MHz, D_2O , pD 7.4, 291 K) recorded for a mixture of an equimolar mixture of **1** – **11** and KCl: A) 1 mM, B) 500 μM , C) 250 μM , D) 100 μM , E) 50 μM .