Supporting Information

Evidence for stereoelectronic effects in ligand exchange reaction on Au_{25} nanoclusters

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Supporting figures

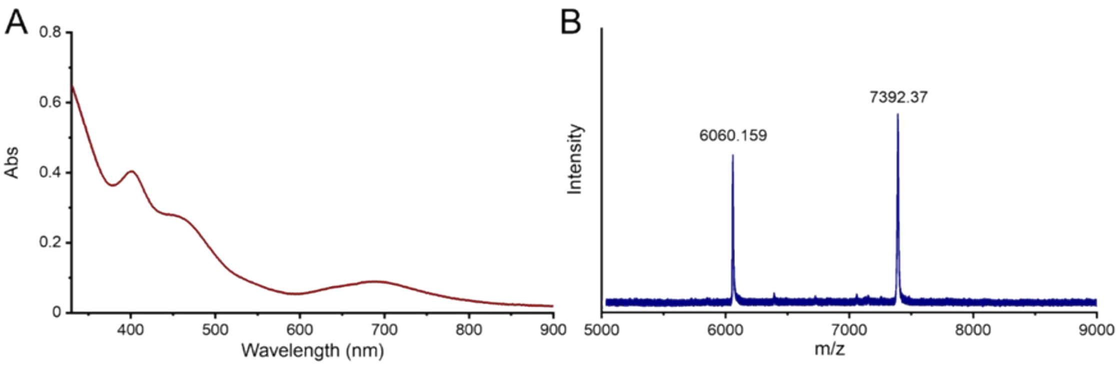


Figure S1. The characterizations of $Au_{25}(2\text{-PET})_{18}$ nanoclusters. (A) UV-vis spectrum, sample dissolved in toluene, and (B) MALDI-TOF Mass spectrum. The signal at 7392.37 corresponds to $Au_{25}(2\text{-PET})_{18}$ (calculated mass 7394.39), the signal at 6060.1589 corresponds to $Au_{21}(2\text{-PET})_{14}$ (loss of $Au_4(2\text{-PET})_4$ ligand, calculated mass 6057.59).

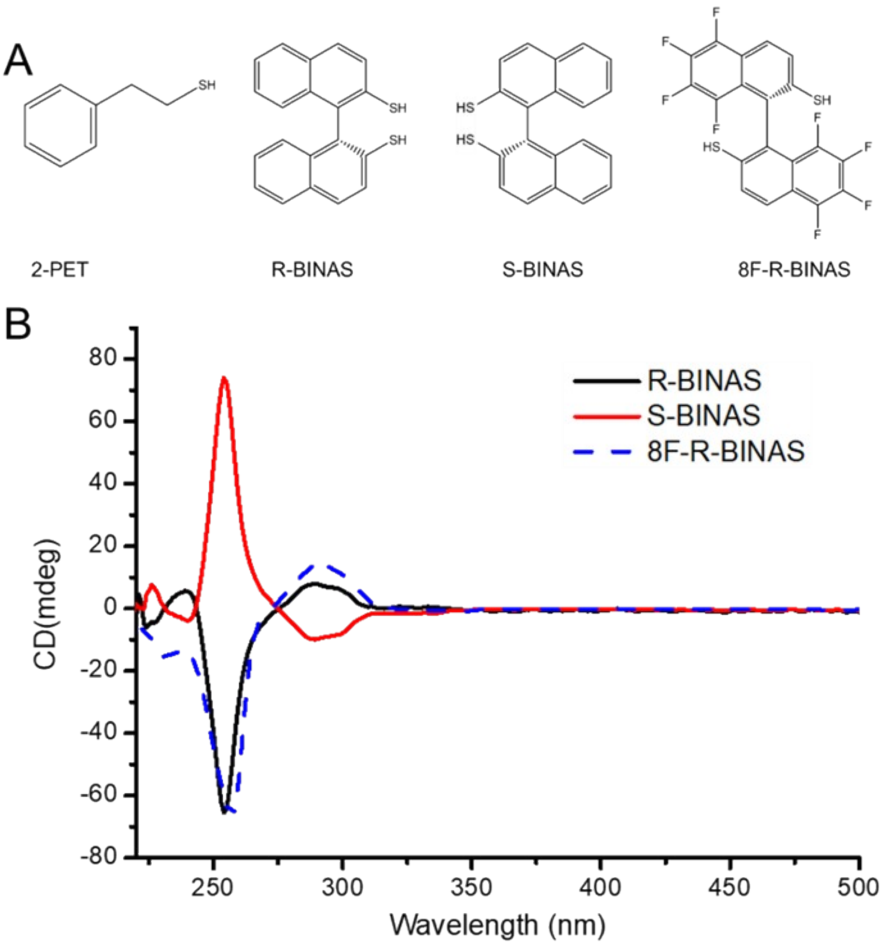
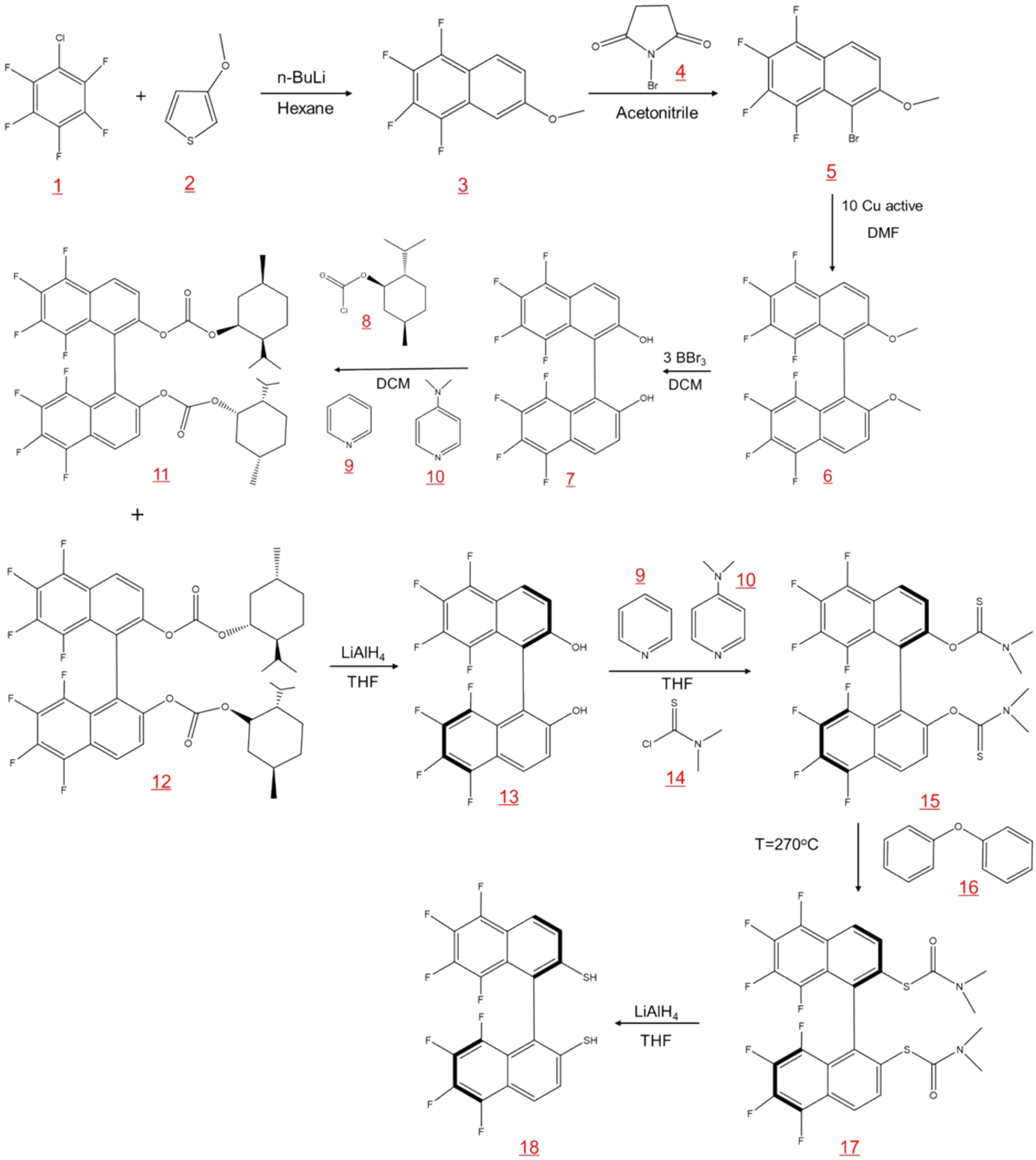


Figure S2. Characterizations of free ligands. (A) Structures of involved ligands in the experiment. 2-PET: 2-phenylethylthiolate, R/S-BINAS: R/S-1,1'-binaphthalene-2,2'-dithiol, 8F-R-BINAS: (R)-5,5',6,6',7,7',8,8'-octafluoro- [1,1'-binaphthalene]-2,2'-dithiol. (B) CD spectra of R/S-BINAS and 8F-R-BINAS, the samples are dissolved in dichloromethane.



Scheme S1. Synthesis of the 8F-R-BINAS: (R)-5,5',6,6',7,7',8,8'-octafluoro- [1,1'-binaphthalene]-2,2'-dithiol. Here the product 7 after reacted under 8,9,10, obtained products 11 and 12 together, for the next reaction just product 12 involved in the reaction. Following are the nomenclatures of corresponding molecules. (1). 1-chloro-2,3,4,5,6-pentafluorobenzene, (2). 3-mthoxythieophene, (3). 1,2,3,4-tetrafluoro-6-methoxynaphthalene, (4). 1-bromopyrrolidine-2,5 -dione, (5). 5-bromo-1,2,3,4-tetrafluoro-6-methoxynaphthalene, (6). 5,5',6,6',7,7',8,8'-octafluoro- 2,2'-dimethoxy-1,1'-binaphthalene, (7). 5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diol, (8). (1R,2S,5R)-2-isopropyl-5-methylcyclohexylcarbonochloridate, (9). Pyridine, (10). N,N-dimethylpyridin-4-amine, (11). bis((1S,2S,5S)-2-isopropyl-5-methylcyclohexyl) (5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl)bis(carbonate), (12). bis((1R,2S,5R)-2- isopropyl-5-methylcyclohexyl)(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl)bis(carbonate), (13). (R)5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diol, (14). Dimethylcarbamothioic chloride, (15). (R)-5,5',6,6',7,7',8,8'- octafluoro-[1,1'-binaphthalene] -2,2'-diyl)bis(dimethylcarbamothioate), (16). Phenyl ether, (17). R'-(5,5',6,6',7,7',8,8' -octafluoro-[1,1'-binaphthalene]-2,2'-diyl)bis(dimethylcarbamothioate), (18). (R)-5,5',6,6',7,7',8,8'- octafluoro- [1,1'-binaphthalene]-2,2'-dithiol.

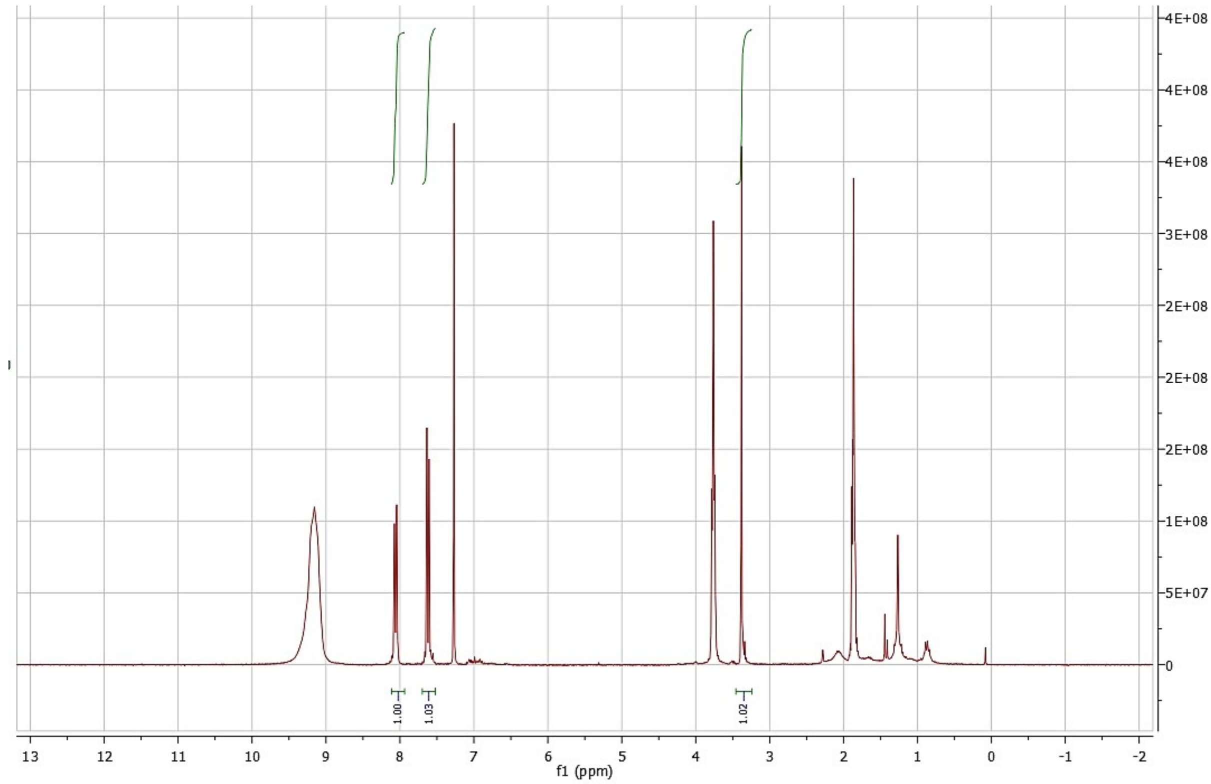


Figure S3. [1]H-NMR spectrum of (R)-5,5',6,6',7,7',8,8'-octafluoro- [1,1'-binaphthalene]-2,2'-dithiol. [1]H-NMR (500 MHz, Chloroform-d) δ 8.05 (2H), 7.61 (2H), 3.37 (2H).

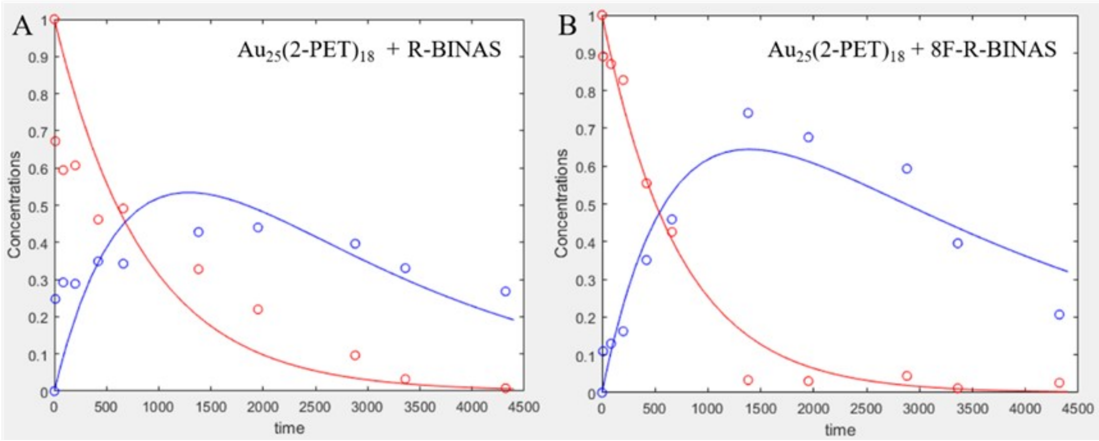


Figure S4. MATLAB simulated concentration plot of the $Au_{25}(2\text{-}PET)_{18}$ reacted with R-BINAS (A) and 8F-R-BINAS (B) separately. Red dots ($Au_{25}(2\text{-}PET)_{18}$) and blue dots (one-exchange species) related to the raw data extracted from Table S2 (A) and Table S3 (B), solid curves corresponding to the fitting results.

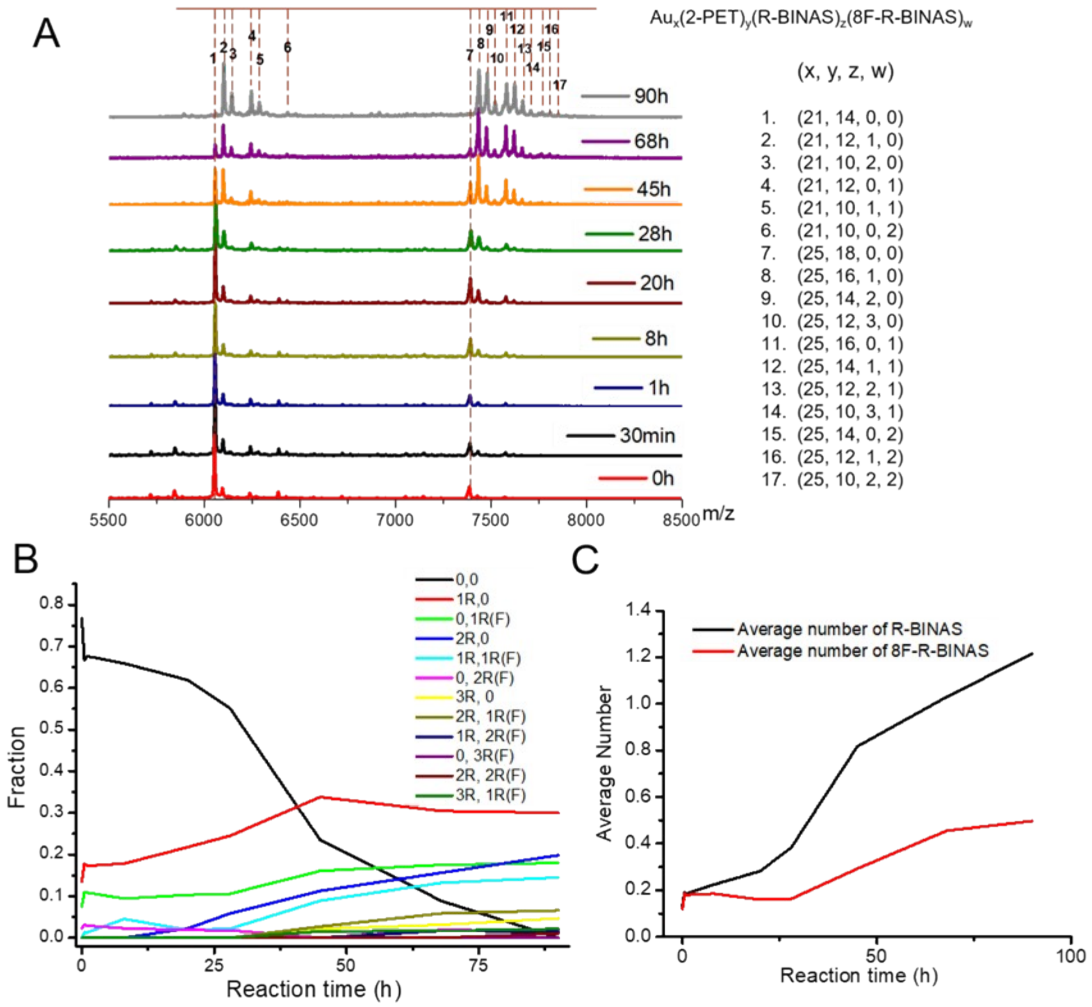


Figure S5. Characterizations of $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with R-BINAS and 8F-R-BINAS mixture. The ratio between clusters and free ligand is 1:15, and the ratio between R-BINAS and 8F-R-BINAS is 1:2. (A) Evolution of MALDI-TOF mass spectra. The compositions of different peaks are exhibited at right side. (B) Evolution of different fractions of $Au_{25}(2\text{-}PET)_{18-2x-2y}(R\text{-}BINAS)_x(8F\text{-}R\text{-}BINAS)_y$ as function of time. (C) Average number of exchanged R-BINAS (black curve) and 8F-R-BINAS (red curve) in the cluster as function of time.

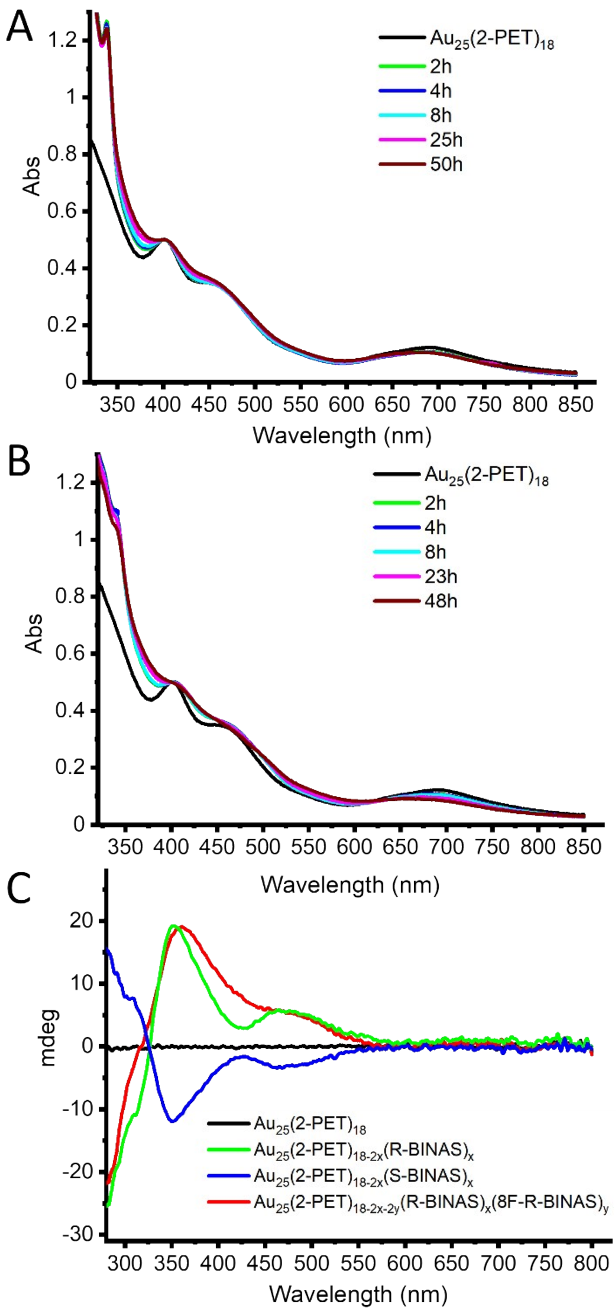


Figure S6. (A) UV-Vis spectra of $Au_{25}(2\text{-}PET)_{18-2x}(R\text{-}BINAS)_x$, $Au_{25}(2\text{-}PET)_{18}$ reacted with R-BINAS (the ratio between clusters and free ligand is 1:20) after 2h (x=0.54), 4h (x=0.61), 8h (x=0.80), 25h (x=1.04) and 50h (x=1.66). (B) UV-Vis spectra of $Au_{25}(2\text{-}PET)_{18-2x-2y}(R\text{-}BINAS)_x(8F\text{-}R\text{-}BINAS)_y$, $Au_{25}(2\text{-}PET)_{18}$ reacted with R-BINAS & 8F-R-BINAS mixture (the ratio between clusters and free ligand is 1:15, and the ratio between R-BINAS and 8F-R-BINAS is 1:4). Spectra recorded at 2h (x=0.10, y=0.11), 4h (x=0.13, y=0.127), 8h (x=0.18, y=0.17), 23h (x=0.30, y=0.26) and 48h (x=0.67, y=0.50). (C) Circular dichroism spectra of $Au_{25}(2\text{-}PET)_{18}$, $Au_{25}(2\text{-}PET)_{18-2x}(R\text{-}BINAS)_x$ (x=1.32) , $Au_{25}(2\text{-}PET)_{18-2x}(S\text{-}BINAS)_x$ (x=1.15) and $Au_{25}(2\text{-}PET)_{18-2x-2y}(R\text{-}BINAS)_x(8F\text{-}R\text{-}BINAS)_y$ (x=1.2, y=0.75).

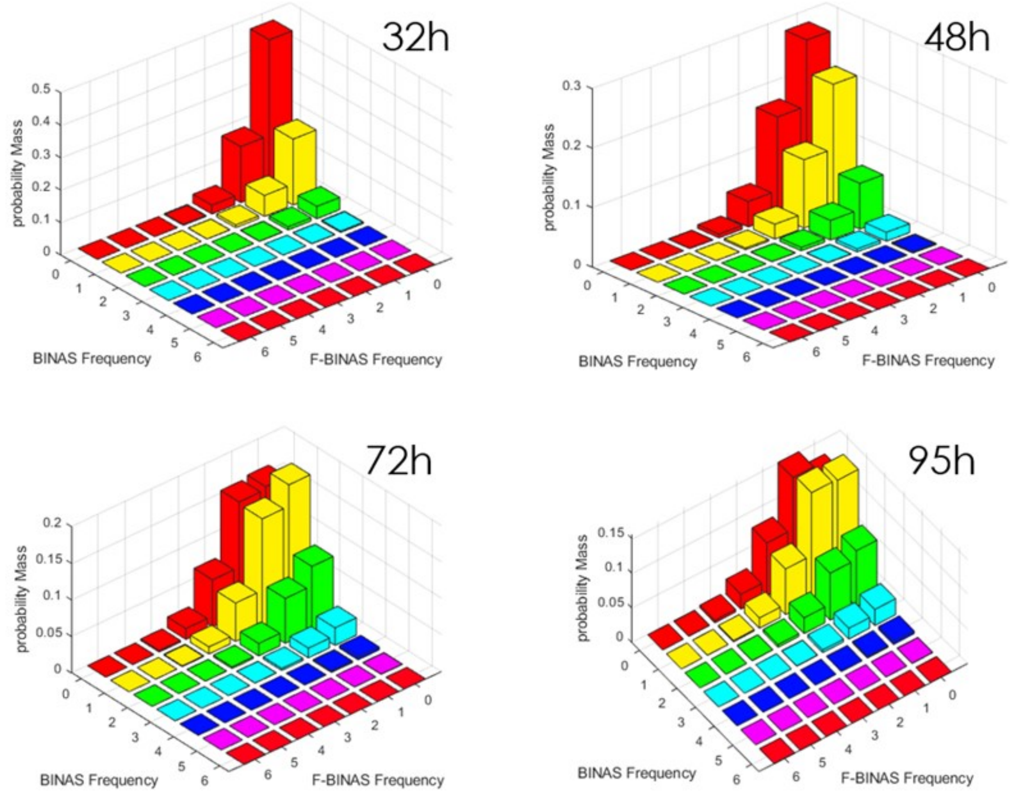


Figure S7. Multinomial distributional diagram of $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with R-BINAS and 8F-R-BINAS mixture at various times. The ratio between clusters and free ligand is 1:15, and the ratio between R-BINAS and 8F-R-BINAS is 1:4.

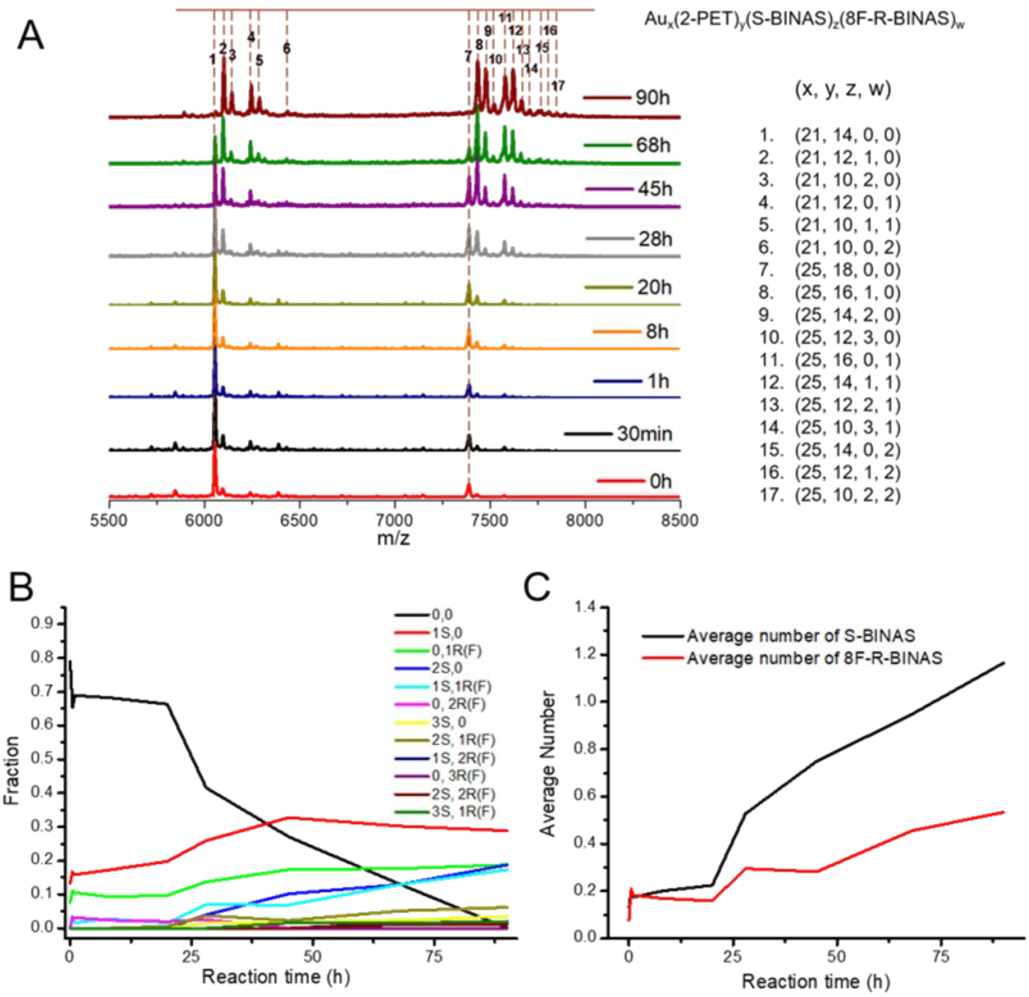
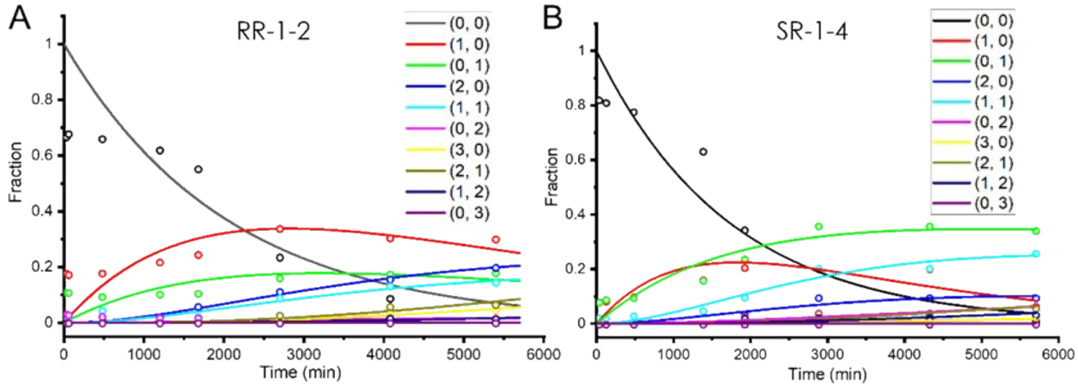
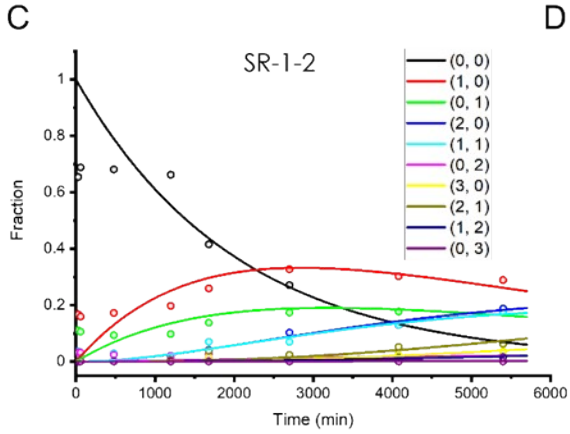


Figure S8. Characterizations of $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with S-BINAS and 8F-R-BINAS mixture. The ratio between clusters and free ligand is 1:15, and the ratio between R-BINAS and 8F-R-BINAS is 1:2. (A) Evolution of MALDI-TOF mass spectra. The compositions of different peaks are exhibited at right side. (B) Evolution of different fractions of $Au_{25}(2\text{-}PET)_{18-2x-2y}(S\text{-}BINAS)_x(8F\text{-}R\text{-}BINAS)_y$ as function of time. (C) Average number of exchanged S-BINAS (black curve) and 8F-R-BINAS (red curve) in the cluster as function of time.





D

Constant	RR-1-4	RR-1-2	SR-1-4	SR-1-2
k1	0.000337	0.000333	0.000333	0.000324
k2	0.000225	0.000156	0.000244	0.000169
k3	0.000192	0.000178	0.00015	0.000152
k4	0.000232	7.11E-05	0.000366	8.73E-05
k5	8.12E-09	0.000145	2.30E-14	0.000136
k6	6.29E-05	3.52E-05	3.99E-05	4.89E-05
k7	8.44E-05	9.44E-05	5.16E-05	8.32E-05
k8	0.000162	2.87E-05	5.09E-05	1.18E-08
k9	9.02E-07	0.00015	5.59E-05	0.000162
k10	4.16E-05	1.63E-05	4.59E-05	2.27E-14
k11	5.23E-05	0.000217	1.77E-09	0.000314
k12	1.41E-05	8.53E-07	6.39E-09	3.65E-05

Figure S9. MATLAB fitting curves of LERs with mixed ligands. (A) Au_{25}(2-PET)$_{18}$ ligand exchange with R-BINAS and 8F-R-BINAS mixture, ratio of two ligands set as 1:2. (B/C) Au_{25}(2-PET)$_{18}$ ligand exchange with S-BINAS and 8F-R-BINAS mixture, ratio of two ligands set as 1:4 and 1:2 separately. (D) The related rate constants of different experiments from MATLAB fitting are listed.

Supporting tables

Table S1. Calculated Mass value of different species after $Au_{25}(2\text{-}PET)_{18}$ ligand exchange reaction with BINAS and 8F-R-BINAS, separately. The fragment signals according to the related species losing $Au_4(2\text{-}PET)_4$.

	$Au_{25}(2\text{-}PET)_{18}$ + BINAS				$Au_{25}(2\text{-}PET)_{18}$ + 8F-R-BINAS			
	Au	2-PET	BINAS	Mass	Au	2-PET	8F-R-BINAS	Mass
Complete signal	25	18	0	7394.39	25	18	0	7394.39
	25	16	1	7436.98	25	16	1	7580.83
	25	14	2	7479.57	25	14	2	7767.22
	25	12	3	7522.16	25	12	3	7953.71
	25	10	4	7564.75	25	10	4	8140.15
	25	8	5	7607.34	25	8	5	8326.59
	25	6	6	7649.93	25	6	6	8513.03
Fragment signal	21	14	0	6057.59	21	14	0	6057.59
	21	12	1	6100.18	21	12	1	6244.03
	21	10	2	6142.77	21	10	2	6430.47
	21	8	3	6185.36	21	8	3	6616.91
	21	6	4	6227.95	21	6	4	6803.35
	21	4	5	6270.54	21	4	5	6989.79
	21	2	6	6313.13	21	2	6	7176.23

Table S2. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with R-BINAS. Data extracted from Figure 1A.

	$Au_{25}(2\text{-}PET)_{18}$ + R-BINAS → $Au_{25}(2\text{-}PET)_{18-2x}(R\text{-}BINAS)_x$							
x	0	1	2	3	4	5	6	Total
Intensity								
10min	582307	214689	62910	6412	0	0	0	866318
85min	766010	376975	124376	13555	7858	0	0	1288774
200min	888029	422482	131333	13742	7574	0	0	1463160
7h	178515	135049	57496	8405	3782	2304	1312	386863
11h	110824	77350	25290	5583	3215	1962	1358	225582
23h	36019	46973	19078	4454	1731	924	640	109819
32.5h	39583	79238	41486	13310	3473	1719	1266	180075
48h	17255	70939	59411	22526	5308	2144	1407	178990
56h	26	263	351	128	27	0	0	795
72h	89	2975	4990	2404	485	105	45	11093

Fraction	0	1	2	3	4	5	6
10min	0.672163	0.247818	0.072618	0.007401	0	0	0
85min	0.594371	0.292507	0.096507	0.010518	0.006097	0	0
200min	0.606925	0.288746	0.08976	0.009392	0.005176	0	0
7h	0.461442	0.349087	0.148621	0.021726	0.009776	0.005956	0.003391
11h	0.49128	0.342891	0.11211	0.024749	0.014252	0.008698	0.00602
23h	0.327985	0.427731	0.173722	0.040558	0.015762	0.008414	0.005828
32.5h	0.219814	0.440028	0.230382	0.073914	0.019286	0.009546	0.00703
48h	0.096402	0.396329	0.331924	0.125851	0.029655	0.011978	0.007861
56h	0.032704	0.330818	0.441509	0.161006	0.033962	0	0
72h	0.008023	0.268187	0.449833	0.216713	0.043721	0.009465	0.004057

Table S3. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with 8F-R-BINAS. Data extracted from Figure 1B.

$Au_{25}(2\text{-}PET)_{18}$ + 8F-R-BINAS → $Au_{25}(2\text{-}PET)_{18-2x}(8F\text{-}R\text{-}BINAS)_x$						
x	0	1	2	3	4	Total
Intensity						
10min	201663	24873	0	0	0	226536
85min	637283	94989	0	0	0	732272
200min	453020	88964	5199	0	0	547183
7h	94320	59750	13894	2145	0	170109
11h	27106	29247	6217	919	229	63718
23h	1631	36307	9230	1512	337	49017
32.5h	778	17156	6374	824	235	25367
48h	2217	29639	15928	1833	356	49973
56h	121	4028	4984	844	208	10185
72h	1319	10458	28428	7852	2505	50562

Fraction	0	1	2	3	4
10min	0.890203	0.109797	0	0	0
85min	0.870282	0.129718	0	0	0
200min	0.827913	0.162585	0.009501	0	0
7h	0.554468	0.351245	0.081677	0.01261	0
11h	0.425406	0.459007	0.097571	0.014423	0.003594
23h	0.033274	0.740702	0.188302	0.030846	0.006875
32.5h	0.03067	0.676312	0.251271	0.032483	0.009264
48h	0.044364	0.5931	0.318732	0.03668	0.007124
56h	0.01188	0.395484	0.489347	0.082867	0.020422
72h	0.026087	0.206835	0.56224	0.155294	0.049543

Table S4. Calculated Mass value of different species after $Au_{25}(2\text{-PET})_{18}$ ligand exchange reaction with mixture of BINAS and 8F-R-BINAS. Maximum 4 ligand exchange species have been calculated here. Fragment signals of $Au_{25}(2\text{-PET})_{18}$ also listed.

$Au_{25}(2\text{-PET})_{18}$ + BINAS+ 8F-R-BINAS → $Au_{25}(2\text{-PET})_{18-2x-2y}(BINAS)_x(8F\text{-}R\text{-}BINAS)_y$					
			x	y	
x+y	Au	2-PET	BINAS (x)	8F-R-BINAS (y)	Mass
0	25	18	0	0	7394.39
1	25	16	1	0	7436.98
	25	16	0	1	7580.83
2	25	14	1	1	7623.42
	25	14	2	0	7479.57
	25	14	0	2	7767.27
3	25	12	3	0	7522.16
	25	12	2	1	7666.01
	25	12	1	2	7809.86
	25	12	0	3	7953.71
4	25	10	4	0	7564.75
	25	10	3	1	7708.6
	25	10	2	2	7852.45
	25	10	1	3	7996.3
	25	10	0	4	8140.15
Fragments of $Au_{25}(2\text{-PET})_{18}$	24	17	0	0	7060.19
	23	16	0	0	6725.99
	22	15	0	0	6391.79
	21	14	0	0	6057.59

Table S5. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-PET})_{18}$ ligand exchange with mixture ligand of R-BINAS and 8F-R-BINAS (molar ratio1:4). Data extracted from Figure 3A.

R-BINAS: 8F-R-BINAS =1:4	$Au_{25}(2\text{-PET})_{18}$ + R-BINAS+ 8F-R-BINAS → $Au_{25}(2\text{-PET})_{18-2x-2y}(R\text{-BINAS})_x(8F\text{-R-BINAS})_y$											
	0-Exchange	1-Exchange		2-Exchange			3-Exchange				4-Exchange	
Intensity	0, 0	1R, 0	0, 1R(F)	2R, 0	1R, 1R(F)	0, 2R(F)	3R, 0	2R, 1R(F)	1R, 2R(F)	0, 3R(F)	2R, 2R(F)	3R, 1R(F)
0h	56201	4918	4495	0	1413	0	0	0	0	0	0	0
30min	84750	5311	3539	0	1535	0	0	0	0	0	0	0
1h	11065	1856	2187	0	976	0	0	0	0	0	0	0
4h	9985	1498	1519	0	773	0	0	0	0	0	0	0
23h	24695	9189	9279	958	3259	0	0	0	0	0	0	0
32h	17727	9545	9046	1294	2717	671	0	721	0	0	0	0
48h	3786	5762	6049	1707	2348	507	430	641	372	0	0	0
72h	1108	12566	19033	6872	10944	3911	1697	2985	1693	0	907	1092
95h	758	6490	22476	8608	17180	5497	2262	4418	2584	0	1192	1426

Fraction	0, 0	1R, 0	0, 1R(F)	2R, 0	1R, 1R(F)	0, 2R(F)	3R, 0	2R, 1R(F)	1R, 2R(F)	0, 3R(F)	2R, 2R(F)	3R, 1R(F)
0h	0.838483	0.073373	0.067063	0	0.021081	0	0	0	0	0	0	0
30min	0.890839	0.055826	0.0372	0	0.016135	0	0	0	0	0	0	0
1h	0.687951	0.115394	0.135974	0	0.060681	0	0	0	0	0	0	0
4h	0.724864	0.108748	0.110272	0	0.056116	0	0	0	0	0	0	0
23h	0.521211	0.193943	0.195842	0.02022	0.068784	0	0	0	0	0	0	0
32h	0.424894	0.228782	0.216821	0.031016	0.065123	0.016083	0	0.017281	0	0	0	0
48h	0.175262	0.266735	0.28002	0.07902	0.108694	0.02347	0.019906	0.029673	0.017221	0	0	0
72h	0.017641	0.20007	0.303035	0.109413	0.174245	0.062269	0.027019	0.047526	0.026955	0	0.014441	0.017386
95h	0.010399	0.089037	0.308351	0.118094	0.235694	0.075414	0.031033	0.060611	0.03545	0	0.016353	0.019563

Table S6. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-PET})_{18}$ ligand exchange with mixture ligand of R-BINAS and 8F-R-BINAS (molar ratio1:2). Data extracted from Figure S5.

R-BINAS: 8F-R-BINAS =1:2	**$Au_{25}(2\text{-PET})_{18}$ + R-BINAS+ 8F-R-BINAS → $Au_{25}(2\text{-PET})_{18-2x-2y}(\text{R-BINAS})_x(\text{8F-R-BINAS})_y$**											
	0-Exchange	1-Exchange		2-Exchange			3-Exchange				4-Exchange	
Intensity	0, 0	1R, 0	0, 1R(F)	2R, 0	1R, 1R(F)	0, 2R(F)	3R, 0	2R, 1R(F)	1R, 2R(F)	0, 3R(F)	2R, 2R(F)	3R, 1R(F)
0h	314626	55210	30493	0	0	9346	0	0	0	0	0	0
30min	286679	76738	47145	0	5865	13797	0	0	0	0	0	0
1h	192340	49159	30843	0	3639	8249	0	0	0	0	0	0
8h	348334	94209	49785	0	23929	12059	0	0	0	0	0	0
20h	183989	64680	30578	6659	5703	5519	0	0	0	0	0	0
28h	66034	29345	12683	6991	2592	2134	0	0	0	0	0	0
45h	8005	11496	5463	3827	3025	0	733	917	0	0	0	518
68h	2249	7755	4461	3986	3369	480	801	1492	434	0	0	435
90h	0	21345	12783	14105	10305	1188	3319	4682	1037	0	791	1509

Fraction	0, 0	1R, 0	0, 1R(F)	2R, 0	1R, 1R(F)	0, 2R(F)	3R, 0	2R, 1R(F)	1R, 2R(F)	0, 3R(F)	2R, 2R(F)	3R, 1R(F)
0h	0.767989	0.134765	0.074432	0	0	0.022813	0	0	0	0	0	0
30min	0.666348	0.178368	0.109582	0	0.013632	0.032069	0	0	0	0	0	0
1h	0.676705	0.172955	0.108514	0	0.012803	0.029022	0	0	0	0	0	0
8h	0.659329	0.178319	0.094233	0	0.045293	0.022825	0	0	0	0	0	0
20h	0.619225	0.217684	0.102912	0.022411	0.019194	0.018574	0	0	0	0	0	0
28h	0.551299	0.244993	0.105887	0.058366	0.02164	0.017816	0	0	0	0	0	0
45h	0.235552	0.338277	0.160752	0.112612	0.089012	0	0.021569	0.026983	0	0	0	0.015242
68h	0.088328	0.304572	0.175202	0.156547	0.132315	0.018852	0.031459	0.058597	0.017045	0	0	0.017084
90h	0	0.300363	0.17988	0.198483	0.14501	0.016717	0.046704	0.065884	0.014592	0	0.011131	0.021234

Table S7. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-PET})_{18}$ ligand exchange with mixture ligand of S-BINAS and 8F-R-BINAS (molar ratio1:4). Data extracted from Figure 5A.

S-BINAS: 8F-R-BINAS =1:4	$Au_{25}(2\text{-PET})_{18}$ + S-BINAS+ 8F-R-BINAS → $Au_{25}(2\text{-PET})_{18-2x-2y}(\text{S-BINAS})_x(\text{8F-R-BINAS})_y$											
	0-Exchange	1-Exchange		2-Exchange			3-Exchange				4-Exchange	
Intensity	0, 0	1S, 0	0, 1R(F)	2S, 0	1S, 1R(F)	0, 2R(F)	3S, 0	2S, 1R(F)	1S, 2R(F)	0, 3R(F)	2S, 2R(F)	3S, 1R(F)
0h	112619	11174	11074	0	3206	0	0	0	0	0	0	0
30min	112619	11174	11074	0	3206	0	0	0	0	0	0	0
2h	356247	37224	39786	0	8742	0	0	0	0	0	0	0
8h	18731	2411	2326	0	762	0	0	0	0	0	0	0
23h	36647	9441	9299	0	2863	0	0	0	0	0	0	0
32h	4821	2896	3334	496	1378	421	0	371	313	0	0	0
48h	4213	5397	6707	1696	2998	711	0	686	534	0	399	0
72h	3092	30300	53732	14533	30638	6229	0	5829	3663	0	2292	0
95h	744	3774	19613	5557	14883	3443	1622	3391	2000	0	1267	1348

Fraction	0, 0	1S, 0	0, 1R(F)	2S, 0	1S, 1R(F)	0, 2R(F)	3S, 0	2S, 1R(F)	1S, 2R(F)	0, 3R(F)	2S, 2R(F)	3S, 1R(F)
0h	0.878667	0.055212	0.046068	0	0.020053	0	0	0	0	0	0	0
30min	0.815648	0.080928	0.080204	0	0.02322	0	0	0	0	0	0	0
2h	0.805991	0.084217	0.090014	0	0.019778	0	0	0	0	0	0	0
8h	0.77305	0.099505	0.095997	0	0.031449	0	0	0	0	0	0	0
23h	0.629133	0.162077	0.159639	0	0.04915	0	0	0	0	0	0	0
32h	0.343621	0.206415	0.237634	0.035353	0.098218	0.030007	0	0.026443	0.022309	0	0	0
48h	0.020571	0.201586	0.357479	0.096688	0.203835	0.041442	0	0.03878	0.02437	0	0.015249	0
72h	0.020571	0.201586	0.357479	0.096688	0.203835	0.041442	0	0.03878	0.02437	0	0.015249	0
95h	0.012907	0.065473	0.340255	0.096405	0.258197	0.059731	0.028139	0.058829	0.034697	0	0.021981	0.023386

Table S8. Mass peak intensity and corresponding fraction of different species after $Au_{25}(2\text{-}PET)_{18}$ ligand exchange with mixture ligand of S-BINAS and 8F-R-BINAS (molar ratio1:2). Data extracted from Figure S8A.

S-BINAS: 8F-R-BINAS =1:2	**$Au_{25}(2\text{-}PET)_{18}$ + S-BINAS+ 8F-R-BINAS → $Au_{25}(2\text{-}PET)_{18-2x-2y}(S\text{-}BINAS)_x(8F\text{-}R\text{-}BINAS)_y$**											
	0-Exchange	1-Exchange		2-Exchange			3-Exchange				4-Exchange	
Intensity	0, 0	1S, 0	0, 1R(F)	2S, 0	1S, 1R(F)	0, 2R(F)	3S, 0	2S, 1R(F)	1S, 2R(F)	0, 3R(F)	2S, 2R(F)	3S, 1R(F)
0h	231153	38823	22375	0	0	0	0	0	0	0	0	0
30min	319483	81371	53896	0	16993	15795	0	0	0	0	0	0
1h	261586	60294	39931	0	5868	11768	0	0	0	0	0	0
8h	183693	46384	25018	0	7563	6462	0	0	0	0	0	0
20h	128239	38183	18797	0	3083	3856	0	1077	0	0	0	0
28h	45562	28418	15044	4382	7649	2792	1600	4090	0	0	0	0
45h	10141	12258	6502	3820	2582	0	678	857	0	0	0	589
68h	7379	17204	10066	7363	7374	922	1364	2923	794	0	618	900
90h	0	18923	12309	12286	11327	1229	2290	4049	971	0	776	1333

Fraction	0, 0	1S, 0	0, 1R(F)	2S, 0	1S, 1R(F)	0, 2R(F)	3S, 0	2S, 1R(F)	1S, 2R(F)	0, 3R(F)	2S, 2R(F)	3S, 1R(F)
0h	0.790669	0.132796	0.076535	0	0	0	0	0	0	0	0	0
30min	0.655299	0.166902	0.110547	0	0.034855	0.032397	0	0	0	0	0	0
1h	0.689387	0.1589	0.105235	0	0.015465	0.031014	0	0	0	0	0	0
8h	0.682569	0.172354	0.092962	0	0.028103	0.024012	0	0	0	0	0	0
20h	0.663643	0.197599	0.097275	0	0.015955	0.019955	0	0.005574	0	0	0	0
28h	0.415951	0.259437	0.137342	0.040005	0.06983	0.025489	0.014607	0.037339	0	0	0	0
45h	0.270954	0.327518	0.173725	0.102065	0.068988	0	0.018115	0.022898	0	0	0	0.015737
68h	0.129668	0.302318	0.176885	0.129387	0.12958	0.016202	0.023969	0.051365	0.013953	0	0.01086	0.015815
90h	0	0.288932	0.187944	0.187593	0.17295	0.018765	0.034966	0.061823	0.014826	0	0.011849	0.020353

Supporting Notes

Note 1. Explicit chemical equations of ligand exchange reaction between $Au_{25}(2\text{-}PET)_{18}$ and R-BINAS or 8F-R-BINAS separately.

Reactional equations for $Au_{25}(2\text{-}PET)_{18}$ + R-BINAS (until 3 exchange):

$$Au_{25}(2-PET)_{18} + R-BINAS \underset{k1}{\rightarrow} Au_{25}(2-PET)_{16}(R-BINAS)_1 + 2-PET$$
$$Au_{25}(2-PET)_{16}(R-BINAS)_1 + R-BINAS \underset{k2}{\rightarrow} Au_{25}(2-PET)_{14}(R-BINAS)_2 + 2-PET$$
$$Au_{25}(2-PET)_{14}(R-BINAS)_2 + R-BINAS \underset{k3}{\rightarrow} Au_{25}(2-PET)_{12}(R-BINAS)_3 + 2-PET$$

Reactional equations for $Au_{25}(2\text{-}PET)_{18}$ + 8F-R-BINAS (until 3 exchange):

$$Au_{25}(2-PET)_{18} + 8F-R-BINAS \underset{k1`}{\rightarrow} Au_{25}(2-PET)_{16}(8F-R-BINAS)_1 + 2-PET$$
$$Au_{25}(2-PET)_{16}(8F-R-BINAS)_1 + 8F-R-BINAS \underset{k2`}{\rightarrow} Au_{25}(2-PET)_{14}(8F-R-BINAS)_2 + 2-PET$$
$$Au_{25}(2-PET)_{14}(8F-R-BINAS)_2 + 8F-R-BINAS \underset{k3`}{\rightarrow} Au_{25}(2-PET)_{12}(8F-R-BINAS)_3 + 2-PET$$

Note 2. Program code of the MATLAB routine for the ligand exchange reaction between Au_{25}(2-PET)$_{18}$ (0,0) and R-BINAS and 8F-R-BINAS up to 2 ligand exchange species.

```
function dydt = kinet(t,y,k)
dydt(1,1) = [-k(1,1)*y(1,1)];
dydt(2,1) = [k(1,1)*y(1,1)] - [k(2,1)*y(2,1)]

function F = myfun(k,xdata)
global ydata
global y0
tspan = [xdata];
ode = @(t,y) kinet(t,y,k);
[t,y] = ode45(ode, tspan, y0);
F=y
```

Kinetic fitting of LERs between Au_{25}(2-PET)$_{18}$ (0,0) and BINAS up to one exchange species, the data were extracted from Table S2.

```
% Fits data to kinetics defined in kinet using least squares in myfun
% dydt = [-x*y(1)]

clear all
type kinet
type myfun
global xdata
global ydata
global y0
% initial concentrations
y0 = zeros(2,1)
y0(1,1) = 1.0
y0(2,1) = 0.0
% Enter data here time, c1, c2
mydata=[0      1.0   0.0
      10   0.672163    0.247818
      85   0.594371    0.292507
     200   0.606925    0.288746
     420   0.461442    0.349087
     660   0.49128     0.342891
    1380   0.327985    0.427731
    1950   0.219814    0.440028
    2880   0.096402    0.396329
    3360   0.032704    0.330818
    4320   0.008023    0.268187
];
  xdata=mydata(:,1);
  ydata(:,1)=mydata(:,2);
  ydata(:,2)=mydata(:,3);

% Time span of the simulation
tspan = [0 4400]

%estimation of kinetic constants
k0 = zeros(2,1)
```

```
k0(1,1) = 0.001
k0(2,1) = 0.001

%x are the fitted parametrs
[k,resnorm] = lsqcurvefit(@myfun,k0,xdata,ydata)

%Solve problem
ode = @(t,y) kinet(t,y,k);
[t,y] = ode45(ode, tspan, y0);

plot(xdata,ydata(:,1),'ro',xdata,ydata(:,2),'bo',t,y(:,1),'r',t,y(:,2),'b')
xlabel('time')
ylabel('Concentrations')

konstants = k
```

Kinetic fitting of LERs between Au_{25}(2-PET)$_{18}$ (0,0) and 8F-R-BINAS up to one exchange species, the data were extracted from Table S3.

```
% Fits data to kinetics defined in kinet using least squares in myfun
% dydt = [-x*y(1)]

clear all
type kinet
type myfun
global xdata
global ydata
global y0
% initial concentrations
y0 = zeros(2,1)
y0(1,1) = 1.0
y0(2,1) = 0.0
% Enter data here time, c1, c2
mydata=[0       1.0   0.0
      10   0.890203    0.109797
      85   0.870282    0.129718
     200   0.827913    0.162585
     420   0.554468    0.351245
     660   0.425406    0.459007
    1380   0.033274    0.740702
    1950   0.03067     0.676312
    2880   0.044364    0.5931
    3360   0.01188     0.395484
    4320   0.026087    0.206835
];
  xdata=mydata(:,1);
  ydata(:,1)=mydata(:,2);
  ydata(:,2)=mydata(:,3);

% Time span of the simulation
tspan = [0 4400]
```

```
%estimation of kinetic constants
k0 = zeros(2,1)
k0(1,1) = 0.001
k0(2,1) = 0.001

%x are the fitted parametrs
[k,resnorm] = lsqcurvefit(@myfun,k0,xdata,ydata)

%Solve problem
ode = @(t,y) kinet(t,y,k);
[t,y] = ode45(ode, tspan, y0);

plot(xdata,ydata(:,1),'ro',xdata,ydata(:,2),'bo',t,y(:,1),'r',t,y(:,2),'b')
xlabel('time')
ylabel('Concentrations')

konstants = k
```

Note 3. Program Code of the MATLAB routine for the multinomial distribution during ligand exchange reaction between $Au_{25}(2\text{-PET})_{18}$ (0,0) and BINAS and F-BINAS.

```
p = [0.06436 0.0667 0.86894];
n = 7;
reps = 10;
rng('default') % for reproducibility

  count1 = 1:n;
  count2 = 1:n;
  [x1, x2]= meshgrid(count1-1, count2-1);
  x3 = n-(x1 + x2);
  y = mnpdf ([x1(:), x2(:), x3(:)], repmat (p, (n)^2, 1));
  y = reshape (y,n,n);
  bar3 (y)
  set (gca, 'XTicklabel', 0:n);
  set (gca, 'YTicklabel', 0:n);
  xlabel ('BINAS Frequency')
  ylabel ('F-BINAS Frequency')
  zlabel ('probability Mass')
```

R-BINAS : 8F-R-BINAS= 1:4					
Probability (7 sites)	Ligand	32h	48h	72h	95h
P1	Normal BINAS	0.05578	0.095679	0.12532	0.12887
P2	Fluor BINAS	0.04734	0.0714	0.10707	0.12552
P3	2-PET	0.89688	0.832921	0.76761	0.74561

Note 4. Program Code of the MATLAB routine for the ligand exchange reaction between $Au_{25}(2\text{-PET})_{18}$ (0,0) and mixed R-BINAS and 8F-R-BINAS ligand. The abbreviations of species were consistent with Scheme 1.

Defined Kinetic file

```
function dydt = kinet(t,y,k)
dydt(1,1) = -[k(1,1)*y(1,1)]-[k(2,1)*y(1,1)];
dydt(2,1) = [k(1,1)*y(1,1)] - [k(3,1)*y(2,1)]-[k(4,1)*y(2,1)];
dydt(3,1) = [k(2,1)*y(1,1)] - [k(5,1)*y(3,1)]-[k(6,1)*y(3,1)];
dydt(4,1) = [k(3,1)*y(2,1)] - [k(7,1)*y(4,1)]-[k(8,1)*y(4,1)];
dydt(5,1) = [k(4,1)*y(2,1)] + [k(5,1)*y(3,1)]- [k(9,1)*y(5,1)]-[k(10,1)*y(5,1)];
dydt(6,1) = [k(6,1)*y(3,1)] - [k(11,1)*y(6,1)]-[k(12,1)*y(6,1)];
dydt(7,1) = [k(7,1)*y(4,1)];
dydt(8,1) = [k(8,1)*y(4,1)] + [k(9,1)*y(5,1)];
dydt(9,1) = [k(10,1)*y(5,1)] + [k(11,1)*y(6,1)];
dydt(10,1) = [k(12,1)*y(6,1)];
```

Defined function file

```
function F = myfun(k,xdata)
global ydata
global y0
tspan = [xdata];
ode = @(t,y) kinet(t,y,k);
[t,y] = ode45(ode, tspan, y0);
F=y;
```

Defined kinetic fitting file

```
clear all
type kinet
type myfun
global xdata
global ydata
global y0

% initial concentrations
y0 = zeros(10,1);
y0(1,1) = 1.0;
y0(2,1) = 0.0;
y0(3,1) = 0.0;
y0(4,1) = 0.0;
y0(5,1) = 0.0;
y0(6,1) = 0.0;
y0(7,1) = 0.0;
y0(8,1) = 0.0;
y0(9,1) = 0.0;
y0(10,1) = 0.0;

% import data from file "data2.txt"

mydata = importdata ('data3.txt')
```

```
  xdata=mydata(:,1);
  ydata(:,1)=mydata(:,2);
  ydata(:,2)=mydata(:,3);
  ydata(:,3)=mydata(:,4);
  ydata(:,4)=mydata(:,5);
  ydata(:,5)=mydata(:,6);
  ydata(:,6)=mydata(:,7);
  ydata(:,7)=mydata(:,8);
  ydata(:,8)=mydata(:,9);
  ydata(:,9)=mydata(:,10);
  ydata(:,10)=mydata(:,11);

% Time span of the simulation
tspan = [0 5700];

% estimation of kinetic constants
k0 = zeros(12,1);
k0(1,1) = 0.009;
k0(2,1) = 0.02;
k0(3,1) = 0.005;
k0(4,1) = 0.001;
k0(5,1) = 0.001;
k0(6,1) = 0.001;
k0(7,1) = 0.001;
k0(8,1) = 0.001;
k0(9,1) = 0.001;
k0(10,1) = 0.001;
k0(11,1) = 0.001;
k0(12,1) = 0.001;

% define lower and upper bounds
lb = [0,0,0,0,0,0,0,0,0,0,0,0]
ub = [1,1,1,1,1,1,1,1,1,1,1,1]

% solve problem
[k,resnorm,residual,exitflag,output,lambda,jacobian] =
lsqcurvefit(@myfun,k0,xdata,ydata,lb,ub);
ci = nlparci(k,residual,'jacobian',jacobian);


% generate kinetic curves with fitted parametrs
ode = @(t,y) kinet(t,y,k);
[t,y] = ode45(ode, tspan, y0);

% plot data
plot(xdata,ydata(:,1),'ro',xdata,ydata(:,2),'bo',xdata,ydata(:,3),'go',xdata,ydata(:,4),'ko',xdata,yd
ata(:,5),'ro',xdata,ydata(:,6),'bo',xdata,ydata(:,7),'go',xdata,ydata(:,8),'ko',t,y(:,1),'r',t,y(:,2),'b',t,
y(:,3),'g',t,y(:,4),'k',t,y(:,5),'r',t,y(:,6),'b',t,y(:,7),'g',t,y(:,8),'k')
xlabel('time')
ylabel('Concentrations')
```

```
% prepare for output writing
kerr = [k,ci]
reswrite = [t,y]
inpwrite = [xdata,ydata]

% write to excel file
% sheet one: fited kinetics
% sheet two: input data
% sheet three: kinetic constants and 95% confidence intervals
xlswrite('results.xls', reswrite, 1, 'A1')
xlswrite('results.xls', inpwrite, 2, 'A1')
xlswrite('results.xls', kerr, 3, 'A1').
```