Supporting Information

Quadruply hydrogen-bonded heteroduplexes based on imide and urea units arrayed with ADDA/DAAD sequence

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Contents

1. General information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). UV/Vis spectra were measured by SHIMADZU UV-2450. $CDCl_3$, acetone-d_6 and DMSO-d_6 were purchased from Cambridge Isotope Laboratories, used for the titration experiments without further drying. CH_2Cl_2 used for UV/Vis titration experiment is HPLC grade. ^{1}H NMR and UV/Vis titration experiments of heterodimer were carried out twice or three times. Dilution experiments of homodimer were carried out twice. The association constants were reported as the averaged values and the errors were the standard deviation.

2. ^{1}H NMR titration and UV/Vis titration procedure

2.1 ^{1}H NMR titration procedure

The titration procedure is exemplified with **1a** and **2a** as follows:

A stock solution of **2a** as the host (2 mM) was prepared (**Solution A**). The other stock solution containing the host **2a** (2 mM) and the guest **1a** (4 mM) was also prepared (**Solution B**). An aliquot of **Solution A** (X μL) was mixed with an aliquot of **Solution B** (Y μL) in NMR tube (X = 500, 450, ⋯⋯, 50, 0; Y = 0, 50,⋯⋯, 450, 500). This provided eleven samples for NMR determination in which the host concentration was maintained constant. Each titration experiment was performed three times. The titration experiment for **9**·**2d** was repeated twice.

2.2 UV/Vis titration procedure

A stock solution of **1b** as the host (40 μM) was prepared (**Solution A**). The other stock solution containing host **1b** (40 μM) and the guest **2a** (800 μM) was also prepared (**Solution B**). To a 1 cm quartz glass cuvette was added **Solution A** (3.0 mL) and the UV/Vis spectrum was recorded. Aliquots of **Solution B** were then added to the cuvette, maintaining the concentration of **1b** constant at 40 μM. After each addition, the spectrum of the resulting solution was recorded. Three

titration experiments were performed and the results were used for K_a calculation.

3. The method for calculating association constants.[1]

All binding data were analysed by solving the Equations (1)-(3) for NMR titration experiments or solving Equation (4) for UV/Vis titration experiments based nonlinear regression analysis:

$$H + G \underset{}{\overset{K_a}{\rightleftharpoons}} HG$$

$$[HG] = \frac{(1/K_a + [G]_0 + [H]_0) - \sqrt{(1/K_a + [G]_0 + [H]_0)^2 - 4[G]_0[H]_0}}{2} \quad (1)$$

$$[H] = [H]_0 - [HG] \quad (2)$$

$$\delta_{obs} = \frac{[HG]}{[H]_0}\delta_b + \frac{[H]}{[H]_0}\delta_f \quad (3)$$

[HG] is the concentration of complex.

$[G]_0$ is the concentration of guest.

$[H]_0$ is the concentration of host.

K_a is the dimerization constant.

δ_f is the free chemical shift of host.

δ_b is the limiting bound chemical shift of host.

δ_{obs} is the observable chemical shift of host.

$$\Delta A = \frac{1}{2}\{(\Delta\varepsilon([H]_0 + [G]_0 + 1/K_a) - \sqrt{\Delta\varepsilon^2([H]_0 + [G]_0 + 1/K_a)^2 - 4\Delta\varepsilon[H]_0[G]_0})\} + \varepsilon_G[G] \quad (4)$$

[HG] is the concentration of complex.

$[G]_0$ is the concentration of guest.

$[H]_0$ is the concentration of host.

K_a is the association constant.

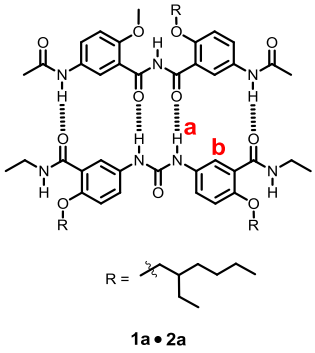
$\Delta\varepsilon$ is the change of molar absorption coeffcient

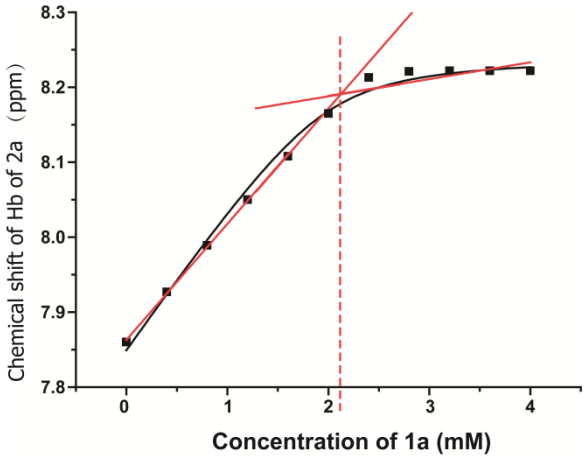
ε_G is the molar absorption coefficient of guest

ΔA is the change of absorption.

4. Self-assembly of duplexes

4.1. Heteroduplex **1a**·**2a**

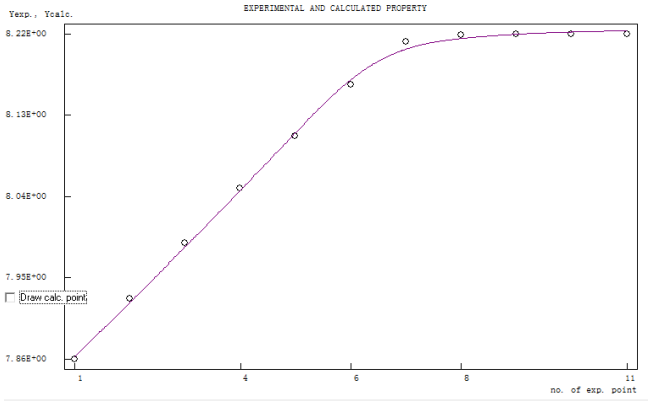




$K_a = (1.6 \pm 0.5) \times 10^4\ M^{-1}$

Figure S1. Determination of the binding constant of **1a**·**2a** in $CDCl_3$ at 298 K. Fitting result based on C-H_b. $\mathbf{K_a}$ is the average value calculated from triplicate measurements, and error is the standard deviation.

The equilibria in the dimeric process include **1a**·**1a**, **2a**·**2a** and **1a**·**2a**. The K_{dim} values of **1a**·**1a** and **2a**·**2a** were obtained by NMR dilution experiments and fixed in the fitting process using ChemEqui 7.23. Chemical shift of **2a** is plotted against number of experimental points corresponding to concentration of **1a**.



$K_a = (8.7 \pm 0.8) \times 10^4\ M^{-1}$

Figure S2. Determination of K_a value of **1a**·**2a** incorporating additional homodimeric equilibria in $CDCl_3$ at 298 K. Fitting result based on C-H_b. $\mathbf{K_a}$ is the average value calculated from triplicate

measurements, and error is the standard deviation.

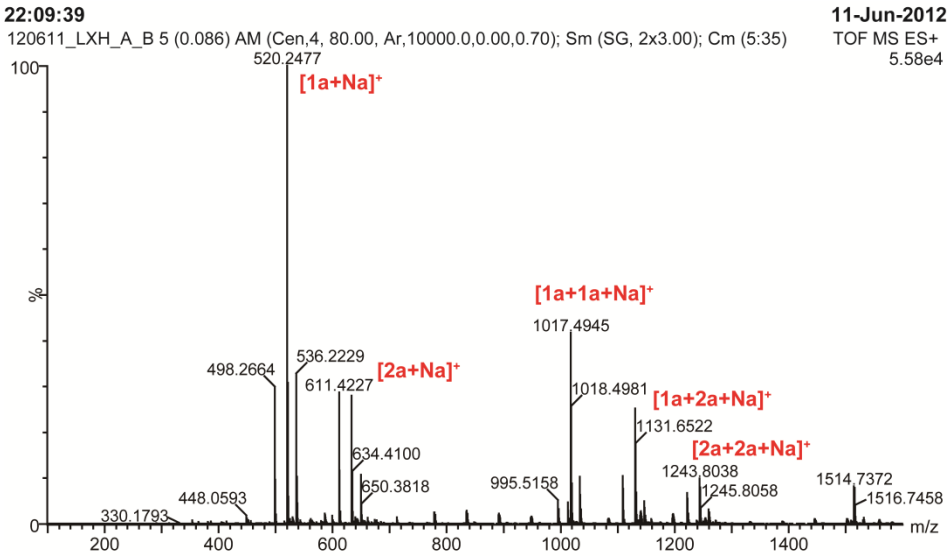
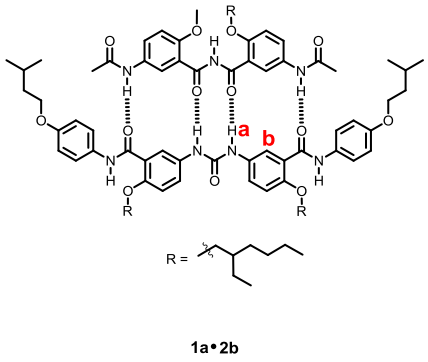
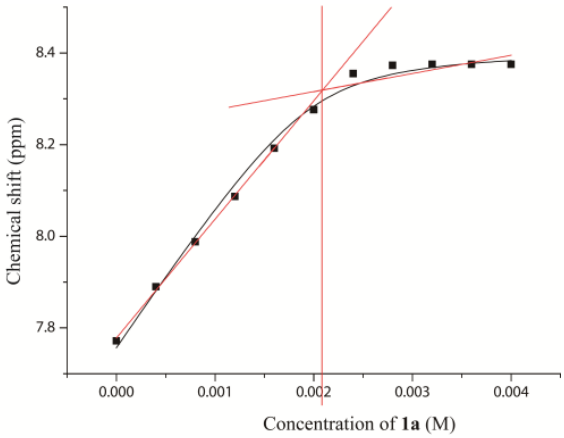


Figure S3. ESI-MS spectrum of **1a** and **2a** (1:1) in CH_3CN.

4.2. Heteroduplex **1a**·**2b**



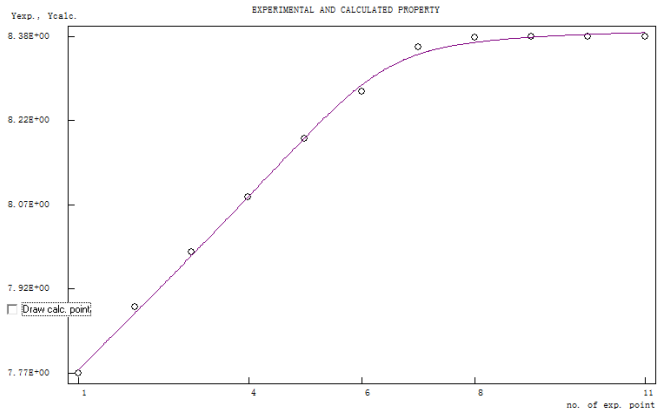
1a•**2b**



$$K_a = (1.9 \pm 0.8) \times 10^4\ M^{-1}$$

Figure S4. Determination of the binding constant of **1a**·**2b** in $CDCl_3$ at 298K. Fitting result based on H_b. $\mathbf{K_a}$ is the average value calculated from triplicate measurements, and error is the standard deviation.

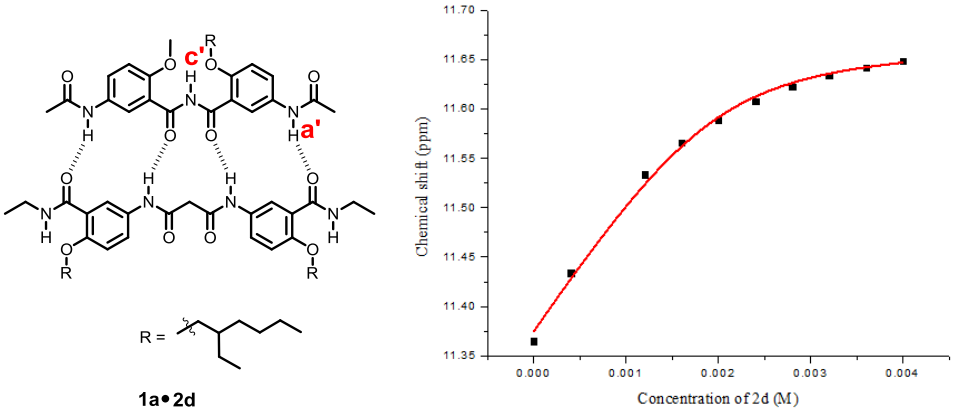
The equilibria in the dimeric process contains **1a**·**1a**, **2b**·**2b** and **1a**·**2b**. The K_{dim} values of **1a**·**1a** and **2b**·**2b** were obtained by NMR dilution experiment, and fixed in the fitting process using ChemEqui 7.23. Chemical shift of **2b** is plotted against number of experimental points corresponding to concentration of **1a**.



$$K_a = (7.4 \pm 2) \times 10^4\ M^{-1}$$

Figure S5. Determination of K_a value of **1a 2b** incorporating additional homodimeric equilibria in $CDCl_3$ at 298 K. Fitting result based on C-H_b. **K_a** is the average value calculated from triplicate measurements, and error is the standard deviation.

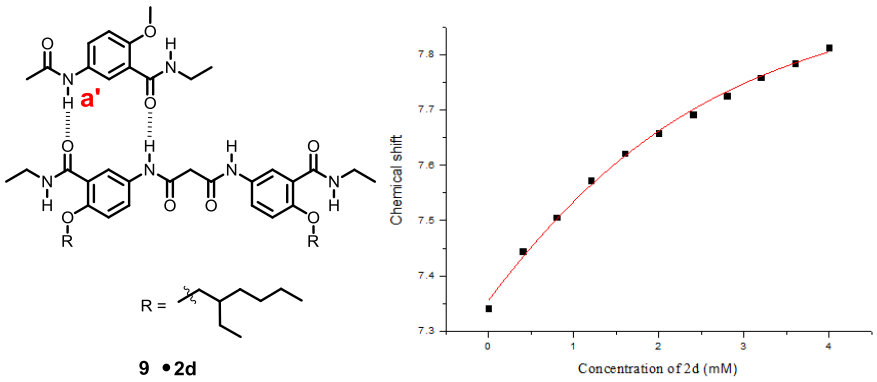
4.3. Heteroduplex **1a 2d**



$$K_a = (4.3 \pm 0.5) \times 10^3\ M^{-1}$$

Figure S6. Determination of the binding constant of **1a 2d** in $CDCl_3$ 298K. Fitting result based on Hc′. **K_a** is the average value calculated from triplicate measurements, and error is the standard deviation.

The following compound **9** with two hydrogen bonds was used to demonstrate that **1a** and **2d** can form a matched heterodimer.



$K_a = 77 \pm 5\ M^{-1}$

Figure S7. Determination of the binding constant of **1a** **2d** in $CDCl_3$ 298K. Fitting result based on Ha′ of **1a**. $\mathbf{K_a}$ is the average value calculated from twice measurements, and error is the standard deviation.

4.4. Heteroduplex **1b** **2a**

(1) Dilution experiment

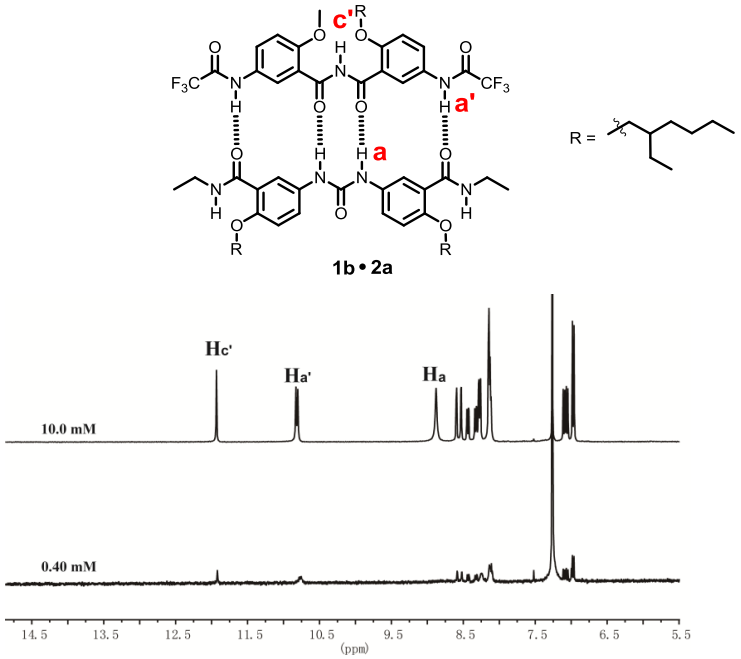


Figure S8. Stacked partial ^{1}H NMR spectra of compounds **1b** and **2a** (1:1) at 0.40 mM and 10.0 mM in $CDCl_3$ (400MHz, 298 K).

(2) UV/Vis experiments for the binding constant

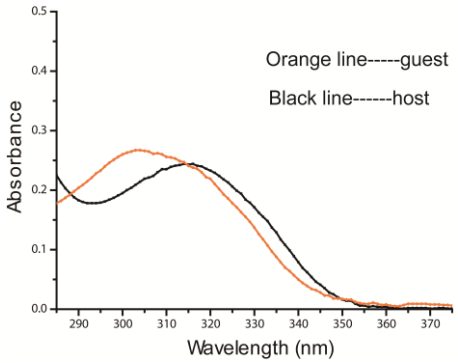


Figure S9. UV/Vis spectra of host **1b** (black line) and guest **2a** (orange line) in CH_2Cl_2.

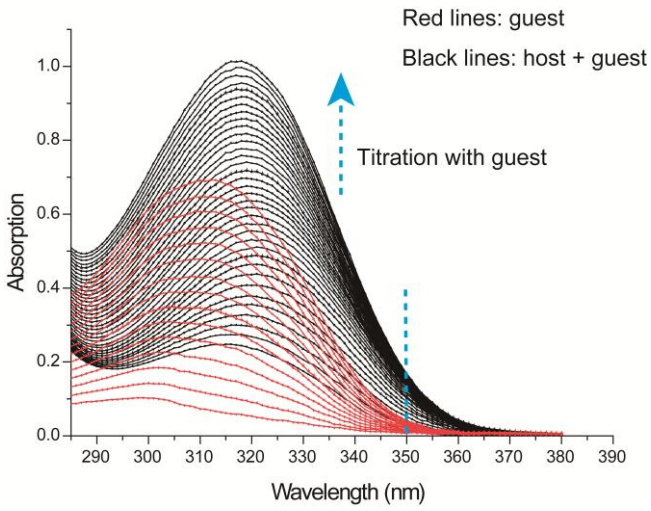
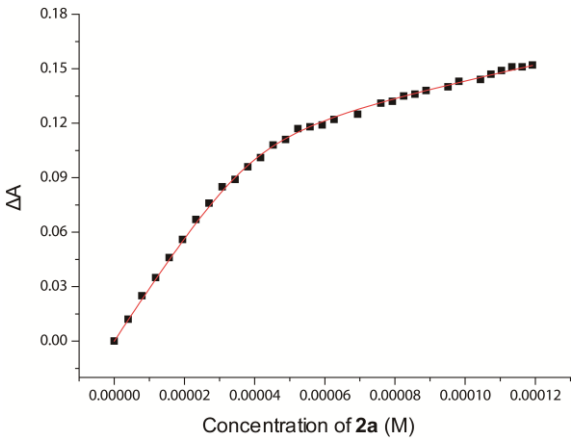


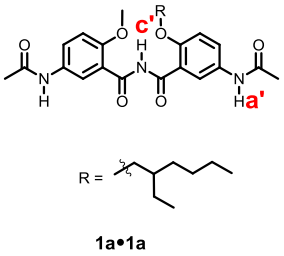
Figure S10. UV/Vis spectra of guest (8-120 μM, red lines) and host (40 μM) titrated with guest (0-3 equiv., black lines).

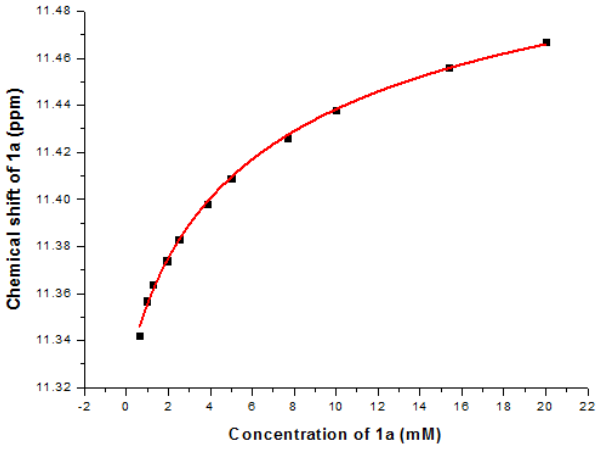


$$K_a = (3.8 \pm 0.7) \times 10^5\ M^{-1}$$

Figure S11. Non-linear curve fitting of ΔA with concentration of **2a** at 350 nm in CH_2Cl_2. $\mathbf{K_a}$ is the average value calculated from triplicate measurements, and error is the standard deviation.

4.5. Homoduplex **1a**•**1a**

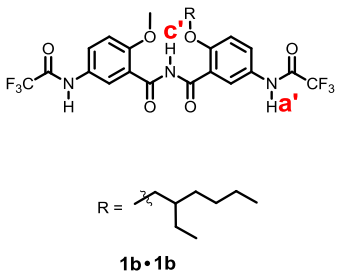


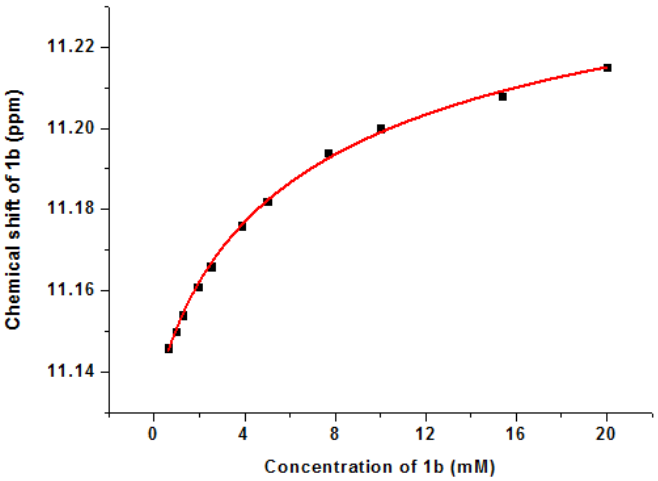


$K_{dim} = 80 \pm 1\ M^{-1}$

Figure S12. Determination of the binding constant of **1a**•**1a** in $CDCl_3$ at 298 K. Fitting result based on Hc′. $\mathbf{K_{dim}}$ is the average value calculated from twice measurements, and error is the standard deviation.

4.6. Homoduplex **1b**•**1b**

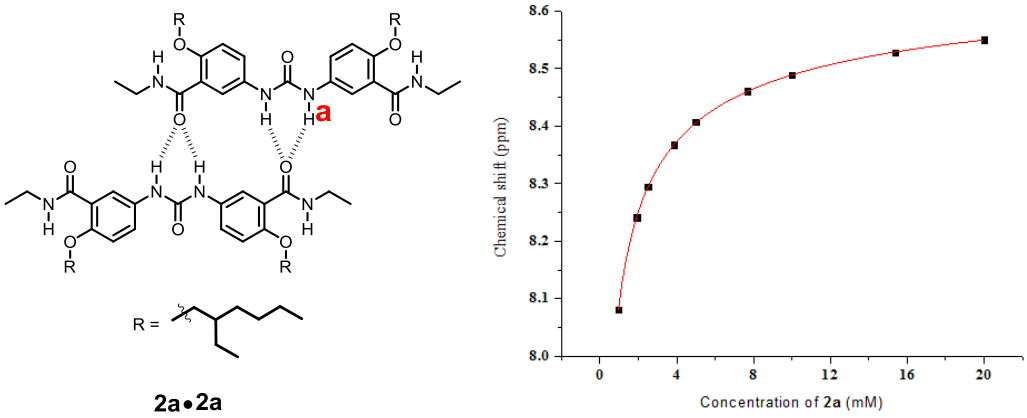




$K_{dim} = 65 \pm 21\ M^{-1}$

Figure S13. Determination of the binding constant of **1b**•**1b** in $CDCl_3$ at 298 K. Fitting result based on Hc′. $\mathbf{K_{dim}}$ is the average value calculated from twice measurements, and error is the standard deviation.

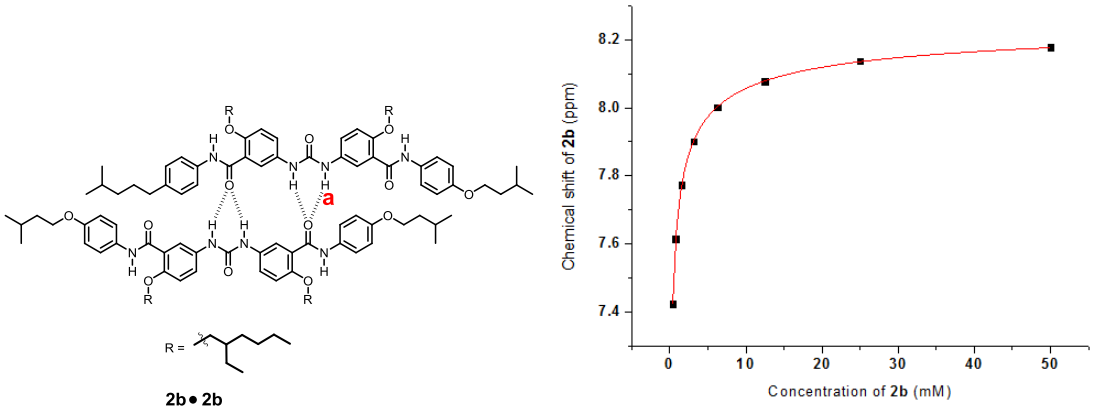
4.7. Homoduplex **2a** ·**2a**



$$K_{dim} = (5.6 \pm 0.1) \times 10^3\ M^{-1}$$

Figure S14. Determination of the binding constant of **2a** ·**2a** in $CDCl_3$ at 298 K. Fitting result based on H_a. $\mathbf{K_{dim}}$ is the average value calculated from twice measurements, and error is the standard deviation.

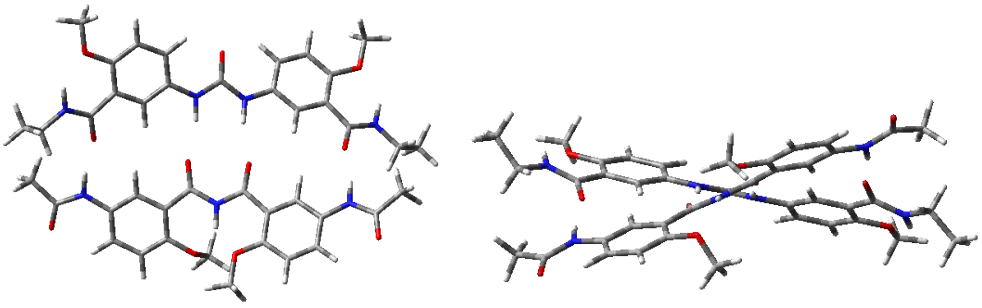
4.8. Homoduplex **2b** ·**2b**



$$K_{dim} = (2.3 \pm 0.4) \times 10^3\ M^{-1}$$

Figure S15. Determination of the binding constant of **2b** ·**2b** in $CDCl_3$ at 298 K. Fitting result based on H_a. $\mathbf{K_{dim}}$ is the average value calculated from twice measurements, and error is the standard deviation.

5. Molecular modelling[2]



Top views Side views

Figure S16 Optimized structure of heterodimer **1a 2a** obtained by DFT calculation at the B3LYP/6-31G(d) level. Substituents are replaced with methyl groups for simplicity.

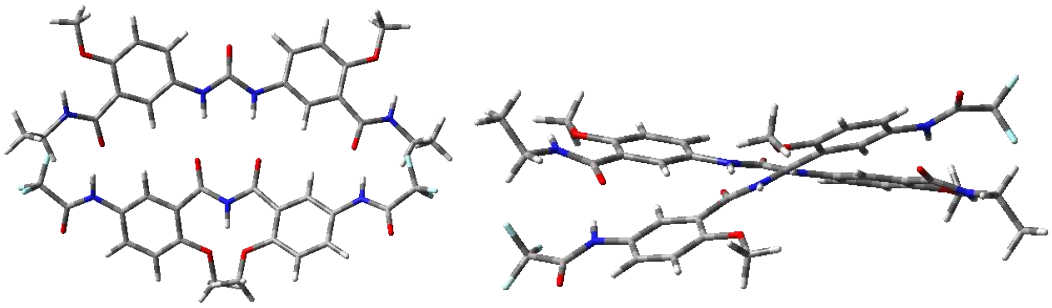
Table S1. Atomic coordinates for the optimized structure of the heterodimer **1a 2a.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.422381	-3.963943	2.045130
2	6	0	4.602972	-2.629605	1.652066
3	6	0	3.504777	-1.929075	1.144116
4	6	0	2.242034	-2.514579	0.996932
5	6	0	2.080100	-3.867070	1.388985
6	6	0	3.171737	-4.563937	1.912356
7	6	0	1.171125	-1.606402	0.460036
8	7	0	0.019207	-2.224041	-0.023182
9	8	0	1.338459	-0.392587	0.423469
10	6	0	-1.148973	-1.606788	-0.453918
11	8	0	-1.339250	-0.398344	-0.388686
12	6	0	-2.218806	-2.524216	-0.984858
13	6	0	-3.509102	-1.982768	-1.042650
14	6	0	-4.598916	-2.706446	-1.539844
15	6	0	-4.391165	-4.017975	-2.002283
16	6	0	-3.112766	-4.564624	-1.947485
17	6	0	-2.030611	-3.843987	-1.444887
18	7	0	5.828151	-1.942172	1.737587
19	7	0	-5.849395	-2.065404	-1.540721
20	8	0	-7.136060	-3.572822	-2.712381
21	8	0	7.107394	-3.441968	2.925156
22	8	0	0.839725	-4.429578	1.247171

23	6	0	0.664784	-5.815335	1.513792
24	8	0	-0.790914	-4.464878	-1.377322
25	6	0	-0.072242	-4.504942	-2.616018
26	6	0	-8.182238	-1.536820	-1.991265
27	6	0	-7.013501	-2.502507	-2.127336
28	6	0	8.105977	-1.338046	2.344601
29	6	0	6.973358	-2.355146	2.372150
30	1	0	5.256562	-4.514432	2.457039
31	1	0	3.627022	-0.894399	0.847421
32	1	0	3.057292	-5.593247	2.231077
33	1	0	0.015661	-3.242384	-0.027781
34	1	0	-3.662658	-0.970402	-0.689041
35	1	0	-5.225495	-4.583364	-2.392352
36	1	0	-2.942719	-5.582145	-2.287565
37	1	0	5.843232	-1.029451	1.282929
38	1	0	-5.874053	-1.166240	-1.059218
39	1	0	0.818110	-6.036438	2.576914
40	1	0	-0.365408	-6.038301	1.234781
41	1	0	1.347307	-6.426365	0.910716
42	1	0	-0.648204	-5.031782	-3.385720
43	1	0	0.160414	-3.492657	-2.969137
44	1	0	0.855228	-5.046244	-2.416962
45	1	0	-8.639234	-1.407990	-2.976720
46	1	0	-8.939714	-1.984253	-1.337778
47	1	0	-7.896290	-0.560998	-1.591039
48	1	0	8.441870	-1.168297	3.372132
49	1	0	8.952157	-1.762665	1.793494
50	1	0	7.824211	-0.383077	1.893970
51	6	0	4.950968	3.817082	-1.374817
52	6	0	4.754879	2.534274	-0.811793
53	6	0	3.456192	2.160155	-0.451692
54	6	0	2.349498	2.995341	-0.642312
55	6	0	2.566338	4.265950	-1.194556
56	6	0	3.854541	4.663739	-1.546475
57	7	0	1.079276	2.498621	-0.302354
58	6	0	-0.041149	3.271207	-0.045470
59	8	0	-0.045326	4.499989	-0.078162
60	7	0	-1.155085	2.504254	0.251226
61	6	0	-2.429119	3.000280	0.575091
62	6	0	-3.517244	2.124364	0.483365
63	6	0	-4.818386	2.496340	0.836408
64	6	0	-5.037622	3.818759	1.288923
65	6	0	-3.960923	4.703848	1.360924
66	6	0	-2.669448	4.309378	1.017035

67	6	0	5.827411	1.511999	-0.542871
68	6	0	-5.868041	1.427362	0.683203
69	8	0	-5.630077	0.396502	0.031835
70	7	0	-7.050189	1.610258	1.318198
71	8	0	5.601486	0.538316	0.194308
72	7	0	7.018372	1.667376	-1.168298
73	8	0	-6.322859	4.185136	1.633005
74	6	0	-6.567365	5.522754	2.045213
75	8	0	6.234046	4.185430	-1.724437
76	6	0	6.456352	5.490883	-2.239358
77	6	0	8.121469	0.730295	-1.015268
78	6	0	-8.128469	0.633002	1.294485
79	6	0	-8.950134	0.691744	2.581044
80	6	0	9.047233	0.773833	-2.229598
81	1	0	3.316071	1.181723	-0.008821
82	1	0	1.733176	4.939691	-1.333958
83	1	0	3.987317	5.652879	-1.967941
84	1	0	1.034378	1.501544	-0.098410
85	1	0	-1.097627	1.498669	0.100442
86	1	0	-3.359485	1.113665	0.127632
87	1	0	-4.111618	5.723064	1.696328
88	1	0	-1.851809	5.012930	1.078311
89	1	0	-7.209210	2.511269	1.751748
90	1	0	7.169355	2.531601	-1.673663
91	1	0	-6.014485	5.768779	2.960384
92	1	0	-6.301994	6.236332	1.255685
93	1	0	-7.639540	5.582573	2.241917
94	1	0	7.531405	5.562442	-2.415541
95	1	0	5.921173	5.647016	-3.184482
96	1	0	6.153687	6.259397	-1.517925
97	1	0	8.690142	0.953455	-0.100116
98	1	0	7.692810	-0.267357	-0.886861
99	1	0	-7.674002	-0.352367	1.166262
100	1	0	-8.779855	0.802182	0.424099
101	1	0	-9.761746	-0.042532	2.547038
102	1	0	-9.404541	1.680419	2.721809
103	1	0	-8.326507	0.475410	3.455096
104	1	0	9.877220	0.071974	-2.098211
105	1	0	8.509371	0.503116	-3.144660
106	1	0	9.478262	1.773161	-2.368767

The total electronic energy is calculated to be -2801.54259639 hartree.



Top views Side view

Figure S17 Optimized structure of heterodimer **1b**·**2a** obtained by DFT calculation at the B3LYP/6-31G(d) level. Substituents are replaced with methyl groups for simplicity.

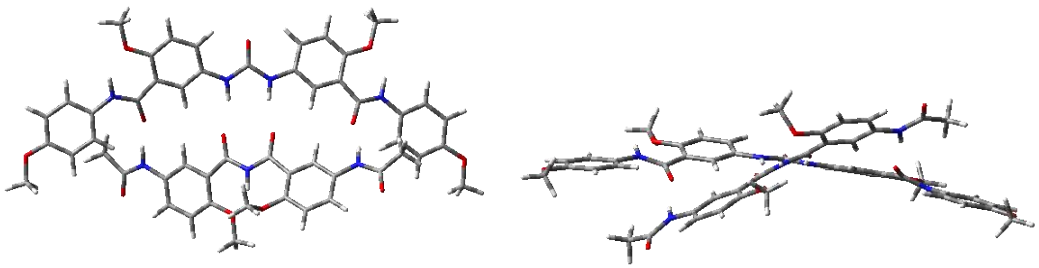
Table S2. Atomic coordinates for the optimized structure of the heterodimer **1b**·**2a.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.510750	-3.791360	1.810796
2	6	0	4.683047	-2.494627	1.308687
3	6	0	3.562110	-1.789823	0.862297
4	6	0	2.278346	-2.343814	0.880922
5	6	0	2.119579	-3.660197	1.379967
6	6	0	3.237810	-4.357183	1.843917
7	6	0	1.179414	-1.434591	0.400188
8	7	0	-0.000025	-2.053306	-0.000123
9	8	0	1.355102	-0.224515	0.335734
10	6	0	-1.179450	-1.434566	-0.400429
11	8	0	-1.355109	-0.224486	-0.335981
12	6	0	-2.278422	-2.343764	-0.881112
13	6	0	-3.562208	-1.789833	-0.862201
14	6	0	-4.683177	-2.494616	-1.308551
15	6	0	-4.510890	-3.791257	-1.810900
16	6	0	-3.237926	-4.357009	-1.844315
17	6	0	-2.119658	-3.660046	-1.380417
18	7	0	5.935842	-1.844410	1.227279
19	7	0	-5.935987	-1.844463	-1.226880
20	8	0	-7.300137	-3.327363	-2.369232
21	8	0	7.299882	-3.327377	2.369678
22	8	0	0.856497	-4.190994	1.392402
23	6	0	0.649409	-5.475313	1.967455
24	8	0	-0.856551	-4.190774	-1.393133
25	6	0	-0.649384	-5.474688	-1.969065
26	6	0	-8.303614	-1.347917	-1.485782
27	6	0	-7.103066	-2.288779	-1.756573

28	6	0	8.303432	-1.347863	1.486466
29	6	0	7.102865	-2.288752	1.757071
30	9	0	-9.217881	-1.468154	-2.450135
31	9	0	-8.888916	-1.668128	-0.308553
32	9	0	-7.936015	-0.047607	-1.412940
33	9	0	9.217637	-1.468202	2.450864
34	9	0	8.888810	-1.667956	0.309239
35	9	0	7.935841	-0.047545	1.413730
36	1	0	5.363425	-4.345832	2.176371
37	1	0	3.685187	-0.783337	0.482428
38	1	0	3.131176	-5.359277	2.241409
39	1	0	-0.000028	-3.068253	-0.000089
40	1	0	-3.685281	-0.783410	-0.482161
41	1	0	-5.363593	-4.345711	-2.176435
42	1	0	-3.131303	-5.359035	-2.241982
43	1	0	5.936911	-0.956681	0.711419
44	1	0	-5.937008	-0.956767	-0.710965
45	1	0	0.948010	-5.489116	3.022198
46	1	0	-0.422633	-5.662381	1.889814
47	1	0	1.198161	-6.253325	1.422268
48	1	0	-1.197796	-6.253168	-1.424202
49	1	0	-0.948323	-5.487878	-3.023719
50	1	0	0.422721	-5.661593	-1.891888
51	6	0	4.987969	3.955327	-1.429937
52	6	0	4.736476	2.609763	-1.070544
53	6	0	3.436947	2.259736	-0.692360
54	6	0	2.380611	3.178244	-0.663784
55	6	0	2.652063	4.507790	-1.017611
56	6	0	3.942997	4.879504	-1.389456
57	7	0	1.109558	2.697826	-0.304550
58	6	0	0.000025	3.468268	-0.000234
59	8	0	0.000044	4.697755	-0.000262
60	7	0	-1.109526	2.697870	0.304105
61	6	0	-2.380555	3.178315	0.663384
62	6	0	-3.436848	2.259764	0.692264
63	6	0	-4.736348	2.609814	1.070518
64	6	0	-4.987866	3.955438	1.429663
65	6	0	-3.942945	4.879658	1.388858
66	6	0	-2.652033	4.507925	1.016946
67	6	0	5.744934	1.490214	-1.045627
68	6	0	-5.744767	1.490225	1.045944
69	8	0	-5.463862	0.405153	0.504825
70	7	0	-6.925740	1.692714	1.671320
71	8	0	5.463938	0.405188	-0.504462

72	7	0	6.926057	1.692701	-1.670722
73	8	0	-6.270460	4.303588	1.799174
74	6	0	-6.549566	5.660223	2.116359
75	8	0	6.270585	4.303476	-1.799368
76	6	0	6.549647	5.660057	-2.116827
77	6	0	7.974305	0.685965	-1.770603
78	6	0	-7.973902	0.685918	1.771524
79	6	0	-8.668027	0.747507	3.131394
80	6	0	8.668263	0.746981	-3.130587
81	1	0	3.254886	1.229433	-0.414075
82	1	0	1.860010	5.241803	-0.990744
83	1	0	4.118836	5.915452	-1.654010
84	1	0	1.050437	1.692875	-0.153752
85	1	0	-1.050408	1.692904	0.153412
86	1	0	-3.254772	1.229412	0.414167
87	1	0	-4.118802	5.915656	1.653205
88	1	0	-1.860013	5.241965	0.989834
89	1	0	-7.105257	2.624498	2.024748
90	1	0	7.105583	2.624442	-2.024257
91	1	0	-5.973021	5.995594	2.987379
92	1	0	-6.339907	6.318346	1.264597
93	1	0	-7.615101	5.698245	2.350184
94	1	0	7.615207	5.698089	-2.350539
95	1	0	5.973182	5.995196	-2.987988
96	1	0	6.339852	6.318359	-1.265237
97	1	0	8.705721	0.820275	-0.963754
98	1	0	7.506085	-0.287239	-1.614866
99	1	0	-7.505558	-0.287315	1.616304
100	1	0	-8.705233	0.819770	0.964524
101	1	0	-9.461984	-0.005035	3.184046
102	1	0	-9.130164	1.727937	3.302371
103	1	0	-7.958992	0.559486	3.944624
104	1	0	9.462301	-0.005496	-3.182973
105	1	0	7.959150	0.558487	-3.943639
106	1	0	9.130262	1.727382	-3.302095

The total electronic energy is calculated to be -3396.96636668 hartree.



Top views Side views

Figure S18 Optimized structure of heterodimer **1a**·**2b** obtained by DFT calculation at the B3LYP/6-31G(d) level. Substituents are replaced with methyl groups for simplicity.

Table S3. Atomic coordinates for the optimized structure of the heterodimer **1a**·**2b.**

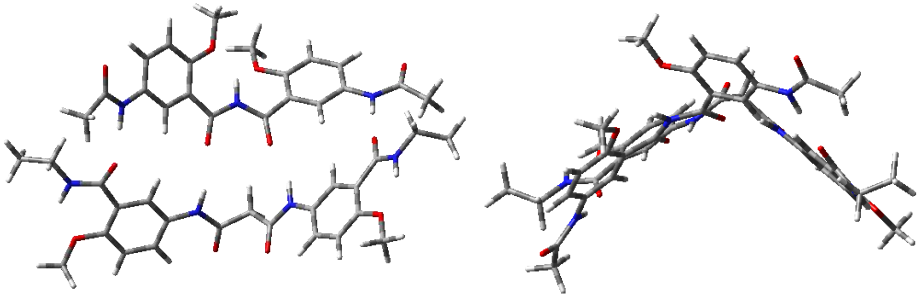
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.165676	-3.872916	-2.037729
2	6	0	-4.344807	-2.498391	-1.824266
3	6	0	-3.316742	-1.779649	-1.208914
4	6	0	-2.127925	-2.380168	-0.779683
5	6	0	-1.973288	-3.775057	-0.982212
6	6	0	-2.990088	-4.492404	-1.617099
7	6	0	-1.119515	-1.438727	-0.182680
8	7	0	-0.012723	-2.014679	0.439446
9	8	0	-1.287864	-0.225131	-0.236146
10	6	0	1.133010	-1.356964	0.870378
11	8	0	1.322994	-0.157268	0.710046
12	6	0	2.185742	-2.217354	1.514952
13	6	0	3.477442	-1.678738	1.533290
14	6	0	4.556711	-2.352289	2.115920
15	6	0	4.333088	-3.604151	2.716249
16	6	0	3.050843	-4.146051	2.704107
17	6	0	1.981285	-3.479310	2.108934
18	7	0	-5.502303	-1.785371	-2.191571
19	7	0	5.812348	-1.724251	2.053314
20	8	0	7.084197	-3.107086	3.380561
21	8	0	-6.585725	-3.328866	-3.506097
22	8	0	-0.815062	-4.361075	-0.547510
23	6	0	-0.674431	-5.775360	-0.604995
24	8	0	0.738336	-4.096823	2.088794
25	6	0	-0.030369	-3.928545	3.285728
26	6	0	8.133962	-1.136836	2.492789
27	6	0	6.974178	-2.101321	2.688446
28	6	0	-7.568213	-1.145430	-3.310876

29	6	0	-6.517631	-2.205934	-3.016941
30	1	0	-4.939962	-4.440075	-2.535319
31	1	0	-3.433569	-0.715077	-1.050873
32	1	0	-2.873905	-5.554715	-1.796602
33	1	0	-0.014834	-3.029426	0.528820
34	1	0	3.641349	-0.711357	1.074717
35	1	0	5.158331	-4.128273	3.177076
36	1	0	2.867798	-5.118358	3.152792
37	1	0	-5.572835	-0.851950	-1.790672
38	1	0	5.843744	-0.888373	1.470883
39	1	0	-0.628136	-6.127039	-1.642580
40	1	0	0.264858	-5.993112	-0.096132
41	1	0	-1.499082	-6.277313	-0.084562
42	1	0	0.508493	-4.324140	4.154890
43	1	0	-0.265173	-2.870635	3.457610
44	1	0	-0.955669	-4.490133	3.140318
45	1	0	9.044405	-1.715045	2.315653
46	1	0	7.984855	-0.433455	1.670050
47	1	0	8.279327	-0.571006	3.420390
48	1	0	-8.558712	-1.560108	-3.103702
49	1	0	-7.439603	-0.226354	-2.734263
50	1	0	-7.529063	-0.907847	-4.379533
51	6	0	-5.105604	4.002566	0.938202
52	6	0	-4.825444	2.690730	0.485800
53	6	0	-3.485322	2.322831	0.317224
54	6	0	-2.421498	3.191776	0.585760
55	6	0	-2.722853	4.487117	1.031662
56	6	0	-4.050151	4.877613	1.196383
57	7	0	-1.112243	2.705165	0.420928
58	6	0	0.021707	3.488844	0.276639
59	8	0	0.005867	4.718110	0.301284
60	7	0	1.169920	2.735836	0.104748
61	6	0	2.465190	3.231544	-0.118761
62	6	0	3.516670	2.306696	-0.160508
63	6	0	4.841295	2.677562	-0.416361
64	6	0	5.123750	4.047609	-0.631655
65	6	0	4.084757	4.975994	-0.572913
66	6	0	2.769763	4.585671	-0.324652
67	6	0	-5.833758	1.623924	0.149287
68	6	0	5.835391	1.548334	-0.440631
69	8	0	5.545938	0.440234	0.036410
70	7	0	7.027836	1.791822	-1.055749
71	8	0	-5.486950	0.598862	-0.454466
72	7	0	-7.113035	1.826945	0.578085

73	8	0	6.431722	4.409535	-0.882632
74	6	0	6.740133	5.784388	-1.072395
75	8	0	-6.426242	4.370040	1.097475
76	6	0	-6.727238	5.683606	1.550499
77	6	0	-8.227171	0.967913	0.442272
78	6	0	8.091887	0.893313	-1.295460
79	6	0	7.949153	-0.498795	-1.318849
80	6	0	9.042915	-1.317640	-1.614053
81	6	0	10.292621	-0.758658	-1.898557
82	6	0	10.436501	0.636447	-1.882242
83	6	0	9.352355	1.446589	-1.582791
84	8	0	11.419180	-1.469533	-2.200531
85	6	0	-9.506339	1.547209	0.511976
86	6	0	-10.649249	0.766232	0.433945
87	6	0	-10.545495	-0.623596	0.276167
88	6	0	-9.277039	-1.209007	0.211773
89	6	0	-8.126533	-0.419953	0.299674
90	8	0	-11.727331	-1.303966	0.197472
91	6	0	11.324217	-2.884164	-2.246623
92	6	0	-11.677688	-2.710255	0.017445
93	1	0	-3.278707	1.318612	-0.031633
94	1	0	-1.923361	5.184989	1.232788
95	1	0	-4.247205	5.887130	1.537019
96	1	0	-1.033022	1.703695	0.250491
97	1	0	1.099226	1.725410	0.210090
98	1	0	3.309339	1.255786	-0.000621
99	1	0	4.283680	6.030247	-0.725067
100	1	0	1.980556	5.321961	-0.285927
101	1	0	7.189769	2.758314	-1.317337
102	1	0	-7.296501	2.742367	0.974117
103	1	0	6.217357	6.195920	-1.944433
104	1	0	6.486981	6.373201	-0.182773
105	1	0	7.817723	5.827413	-1.240592
106	1	0	-7.816167	5.739034	1.599850
107	1	0	-6.306542	5.869662	2.546200
108	1	0	-6.355772	6.439819	0.848852
109	1	0	6.985923	-0.942069	-1.108549
110	1	0	8.897773	-2.391873	-1.623226
111	1	0	11.409263	1.063269	-2.104904
112	1	0	9.479913	2.526786	-1.569235
113	1	0	-9.601586	2.625091	0.622951
114	1	0	-11.636999	1.213185	0.485480
115	1	0	-9.162576	-2.281125	0.099093
116	1	0	-7.152102	-0.885948	0.255887

117	1	0	12.321312	-3.242969	-2.508390
118	1	0	10.607643	-3.216165	-3.009723
119	1	0	11.032814	-3.302026	-1.273781
120	1	0	-12.716178	-3.042512	-0.033800
121	1	0	-11.179254	-3.208885	0.859466
122	1	0	-11.163975	-2.980106	-0.914868

The total electronic energy is calculated to be -3335.43542298 hartree.



Top views Side views

Figure S19 Optimized structure of heterodimer **1a 2d** obtained by DFT calculation at the B3LYP/6-31G(d) level. Substituents are replaced with methyl groups for simplicity.

Table S4. Atomic coordinates for the optimized structure of the heterodimer **1a 2d.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.961163	-2.507628	1.315083
2	6	0	4.929934	-3.798900	1.895540
3	6	0	3.924424	-4.694487	1.523332
4	6	0	2.932857	-4.342712	0.607904
5	6	0	2.939635	-3.063511	0.036984
6	6	0	3.963894	-2.182023	0.394433
7	7	0	1.979155	-2.593358	-0.874901
8	6	0	0.968327	-3.299875	-1.478593
9	6	0	0.186609	-2.452164	-2.495726
10	8	0	0.730061	-4.482086	-1.276679
11	6	0	5.968309	-1.417397	1.582419
12	8	0	5.980497	-0.386016	0.890164
13	7	0	6.822725	-1.591320	2.618713
14	6	0	7.835796	-0.615411	2.995358
15	6	0	-1.250335	-2.933090	-2.654522
16	8	0	-1.558732	-3.790983	-3.469000
17	7	0	-2.137104	-2.310441	-1.803673
18	6	0	4.790665	3.613428	-2.245707

19	6	0	4.882655	2.447328	-1.469364
20	6	0	3.696559	1.800448	-1.104159
21	6	0	2.437497	2.288773	-1.465651
22	6	0	2.360562	3.473841	-2.231036
23	6	0	3.542390	4.109542	-2.619204
24	6	0	1.261021	1.457059	-1.041651
25	7	0	0.110608	2.155820	-0.713752
26	8	0	1.359871	0.240745	-0.921359
27	6	0	-1.085976	1.625862	-0.217566
28	8	0	-1.388672	0.447212	-0.348253
29	6	0	-1.965551	2.584773	0.543796
30	6	0	-3.044063	1.995252	1.215806
31	6	0	-3.897238	2.719524	2.054555
32	6	0	-3.667201	4.092220	2.219796
33	6	0	-2.613867	4.704761	1.545473
34	6	0	-1.762630	3.979165	0.710092
35	7	0	6.096174	1.882098	-1.038215
36	7	0	-4.938316	2.022398	2.695585
37	8	0	-5.500540	3.512560	4.355955
38	8	0	7.625935	3.274949	-2.046861
39	8	0	1.109803	3.927650	-2.561480
40	6	0	0.996299	5.012952	-3.471247
41	8	0	-0.729492	4.573944	0.027004
42	6	0	-0.438747	5.947288	0.253927
43	6	0	-6.593592	1.374885	4.359430
44	6	0	-5.632076	2.420957	3.812572
45	6	0	8.473399	1.436524	-0.756513
46	6	0	7.369670	2.299738	-1.348838
47	6	0	9.247988	-1.020315	2.560752
48	8	0	5.909627	-4.124883	2.807767
49	6	0	5.898997	-5.418635	3.398267
50	6	0	-5.629927	-1.912167	-0.622299
51	6	0	-6.303028	-2.894605	-1.385992
52	6	0	-5.574524	-3.692579	-2.268982
53	6	0	-4.199854	-3.530447	-2.430925
54	6	0	-3.519365	-2.551514	-1.692779
55	6	0	-4.249782	-1.769712	-0.791692
56	6	0	-6.263503	-0.975912	0.371050
57	8	0	-5.560865	-0.359109	1.188441
58	7	0	-7.603134	-0.797214	0.301910
59	6	0	-8.327759	0.117754	1.172243
60	6	0	-9.671060	0.501165	0.555396
61	8	0	-7.664791	-3.026813	-1.215637
62	6	0	-8.349320	-4.045794	-1.932483

63	1	0	3.894640	-5.689437	1.951069
64	1	0	2.158640	-5.046188	0.334519
65	1	0	4.009946	-1.198121	-0.055650
66	1	0	1.992751	-1.590117	-1.039312
67	1	0	0.670141	-2.585420	-3.469527
68	1	0	0.232095	-1.392082	-2.229406
69	1	0	6.784249	-2.479431	3.102926
70	1	0	7.799165	-0.487288	4.084420
71	1	0	7.549066	0.334402	2.540497
72	1	0	-1.777184	-1.549045	-1.233585
73	1	0	5.696559	4.117839	-2.550525
74	1	0	3.741312	0.897341	-0.505962
75	1	0	3.506577	5.008834	-3.223030
76	1	0	0.165868	3.169856	-0.743568
77	1	0	-3.193466	0.928988	1.093633
78	1	0	-4.302671	4.663766	2.881534
79	1	0	-2.465508	5.769069	1.682962
80	1	0	6.013916	1.067187	-0.431857
81	1	0	-5.162903	1.110476	2.295784
82	1	0	-0.073900	5.152686	-3.632416
83	1	0	1.484341	4.783442	-4.426307
84	1	0	1.425738	5.935393	-3.058817
85	1	0	-0.220638	6.138045	1.311301
86	1	0	0.446420	6.161688	-0.346494
87	1	0	-1.267040	6.588184	-0.071287
88	1	0	-7.599993	1.803666	4.403646
89	1	0	-6.297379	1.141158	5.387296
90	1	0	-6.613847	0.451773	3.775035
91	1	0	9.061374	1.013329	-1.577832
92	1	0	8.099005	0.627918	-0.124626
93	1	0	9.144492	2.077616	-0.176023
94	1	0	9.976349	-0.265990	2.880140
95	1	0	9.307123	-1.117383	1.471885
96	1	0	9.540241	-1.979778	3.003384
97	1	0	6.754942	-5.443445	4.074980
98	1	0	6.011632	-6.202504	2.639868
99	1	0	4.977744	-5.590088	3.968144
100	1	0	-6.070556	-4.458412	-2.853472
101	1	0	-3.652418	-4.149953	-3.126384
102	1	0	-3.745678	-1.012642	-0.201681
103	1	0	-8.122338	-1.408794	-0.315649
104	1	0	-8.481251	-0.336305	2.162056
105	1	0	-7.704254	1.003513	1.323508
106	1	0	-10.209054	1.187856	1.216783

107	1	0	−9.532751	0.995079	−0.412414
108	1	0	−10.307603	−0.379282	0.403547
109	1	0	−9.393808	−3.977180	−1.622990
110	1	0	−8.279004	−3.890851	−3.016209
111	1	0	−7.958965	−5.038781	−1.679717

The total electronic energy is calculated to be -2954.18631365 hartree.

6. ^{1}H NMR and ^{13}C NMR of compounds 1a, 1b and 2a-2d

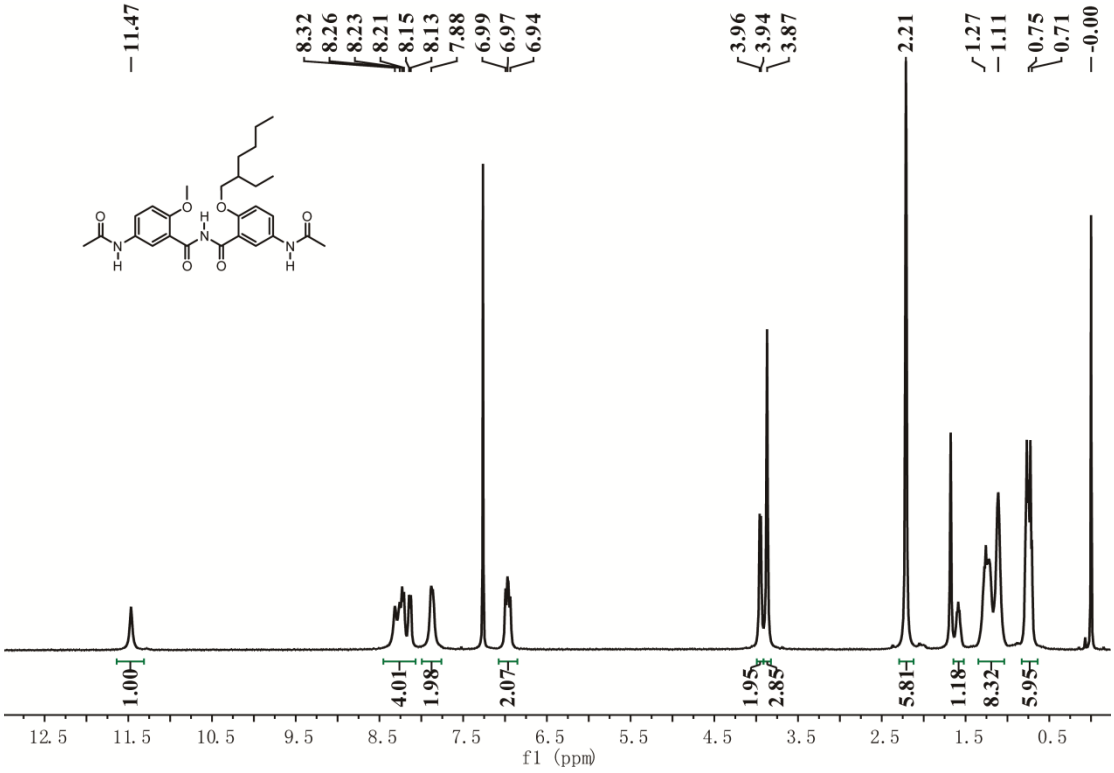


Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**.

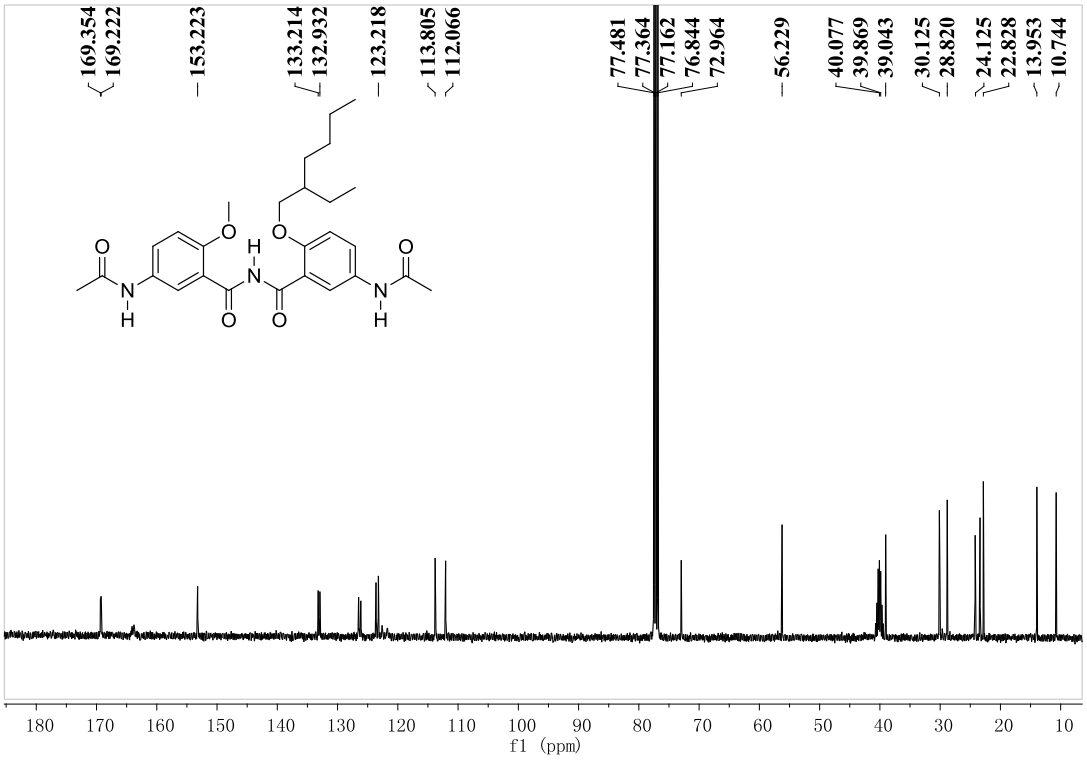


Figure S21. ^{13}C NMR spectrum (100 MHz, $CDCl_3$/DMSO-d_6) of **1a**.

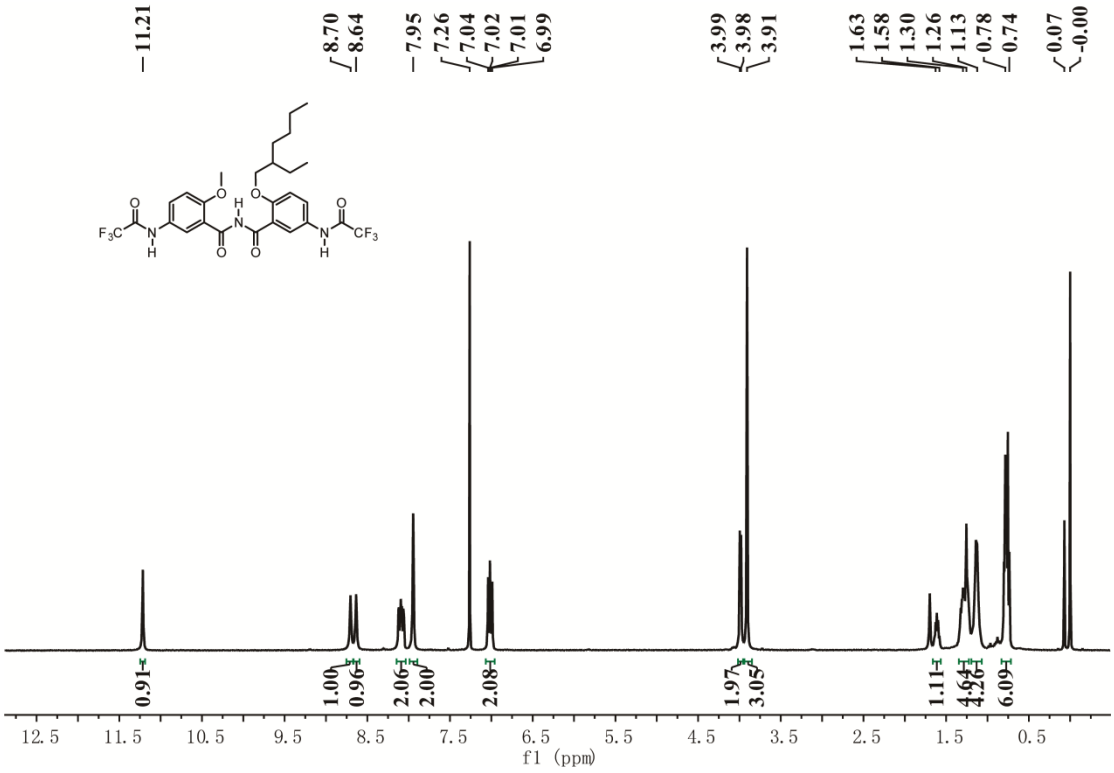


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**.

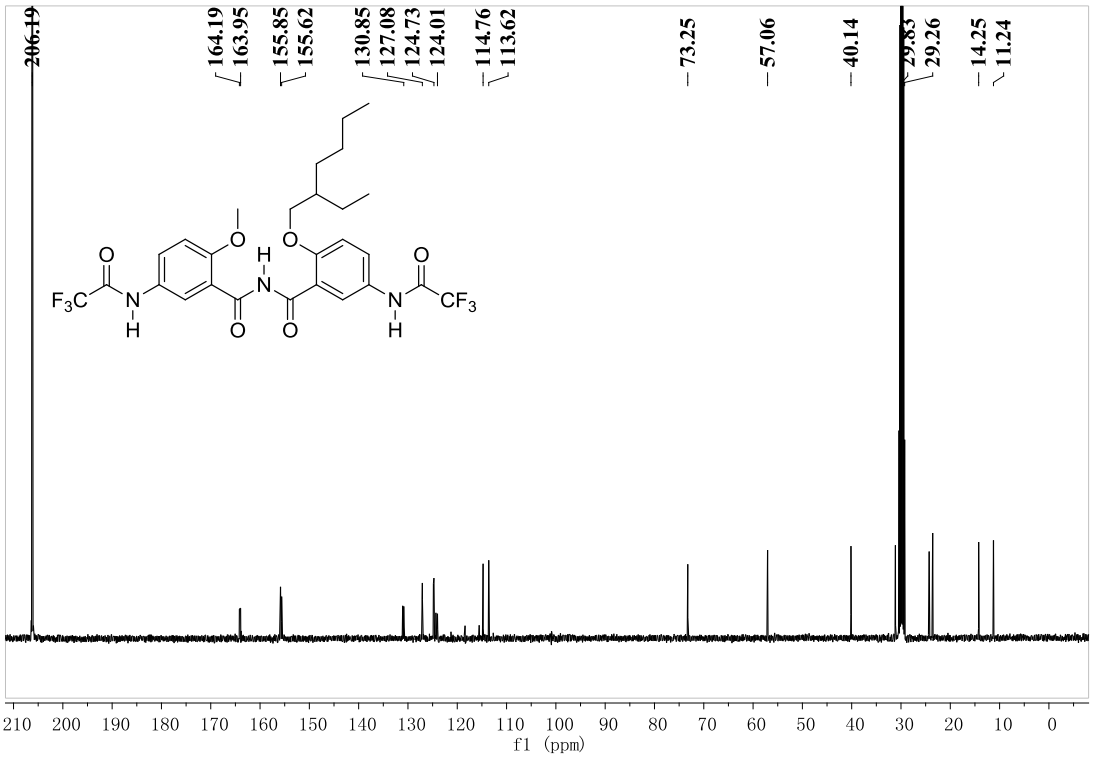


Figure S23. ^{13}H NMR spectrum (100 MHz, acetone-d_6) of **1b**.

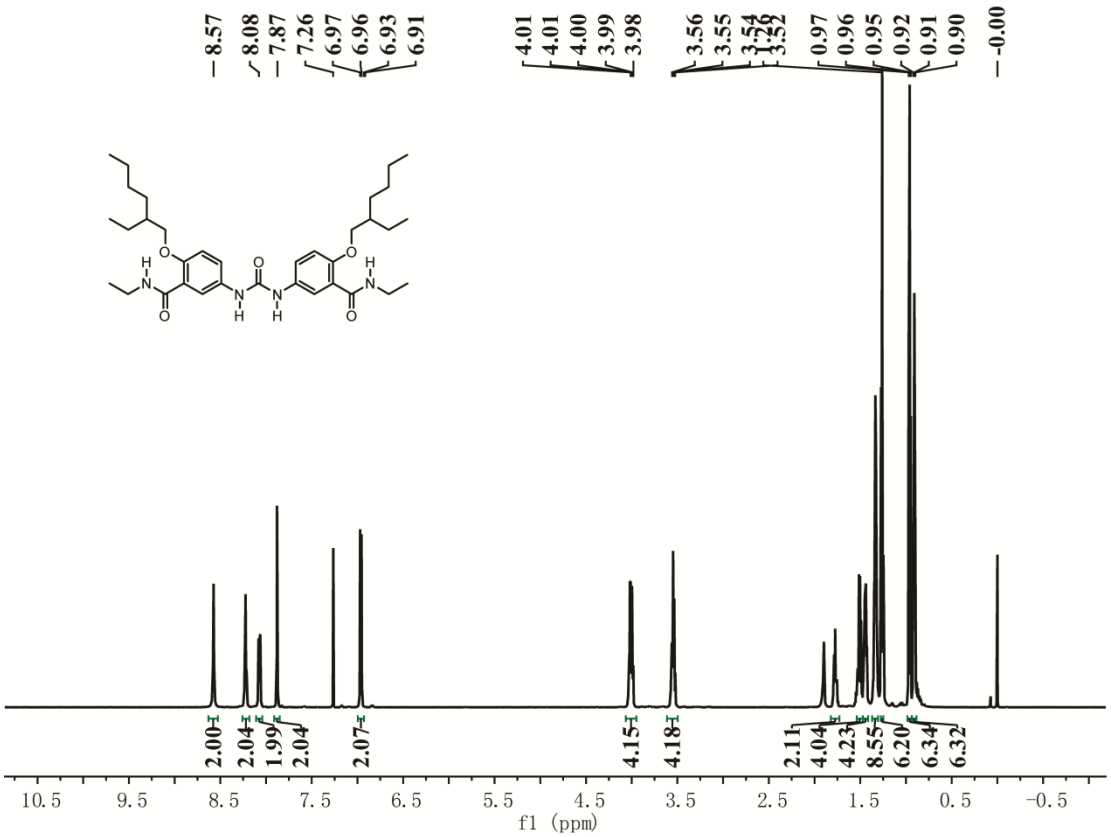


Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a.**

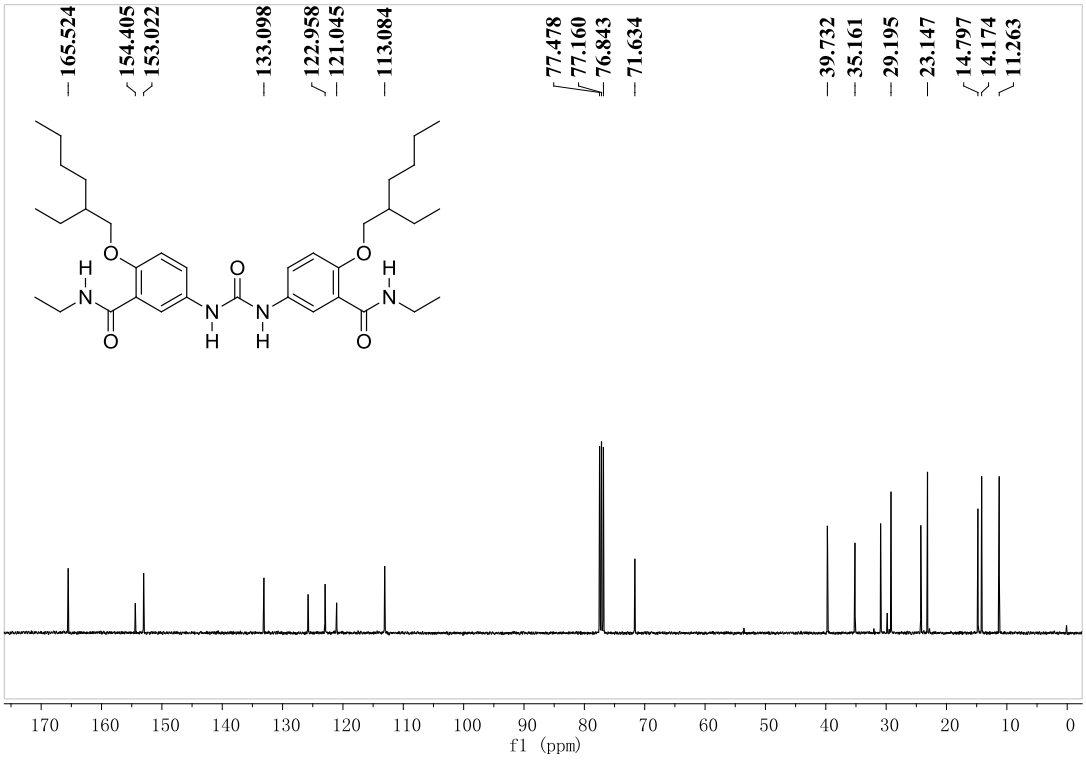


Figure S25. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2a.**

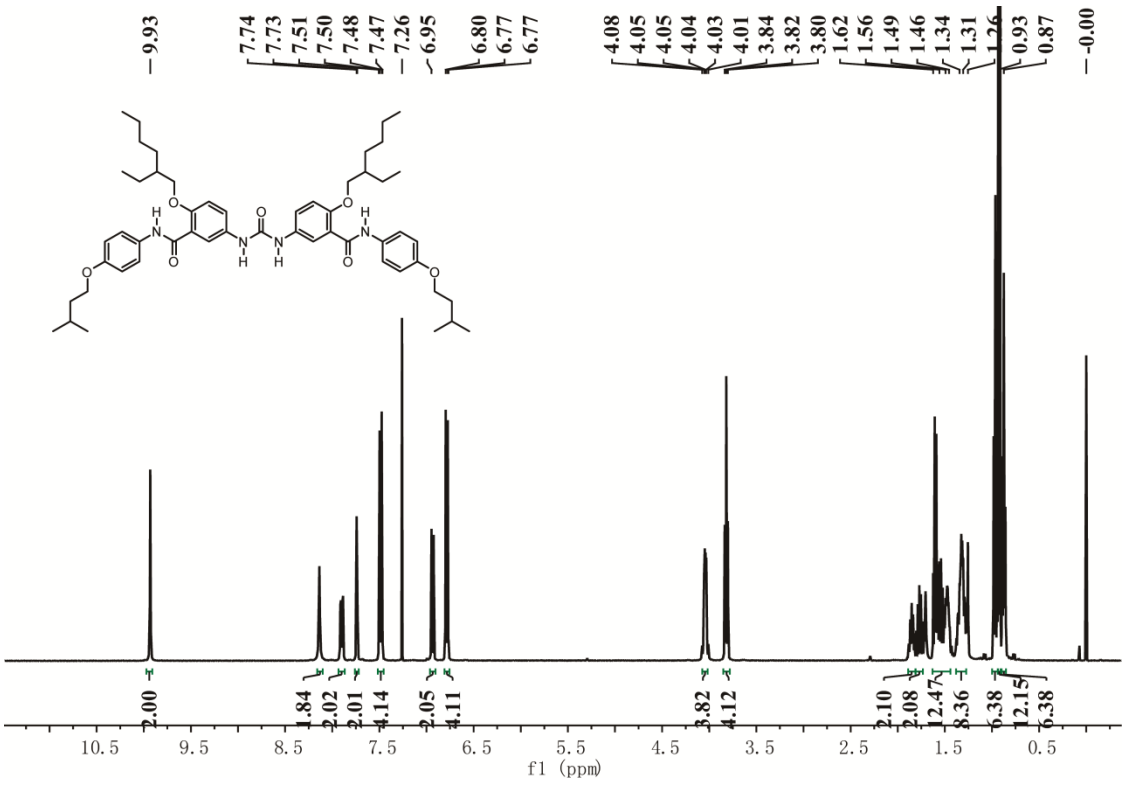


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b.**

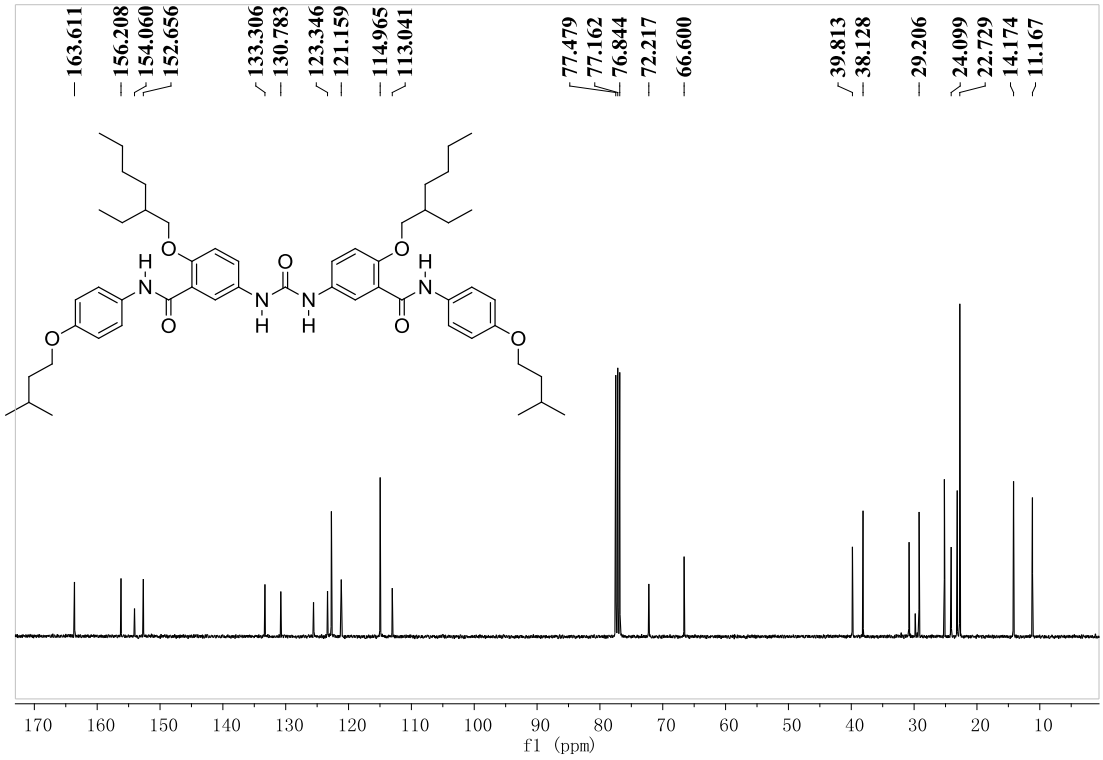


Figure S27. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2b.**

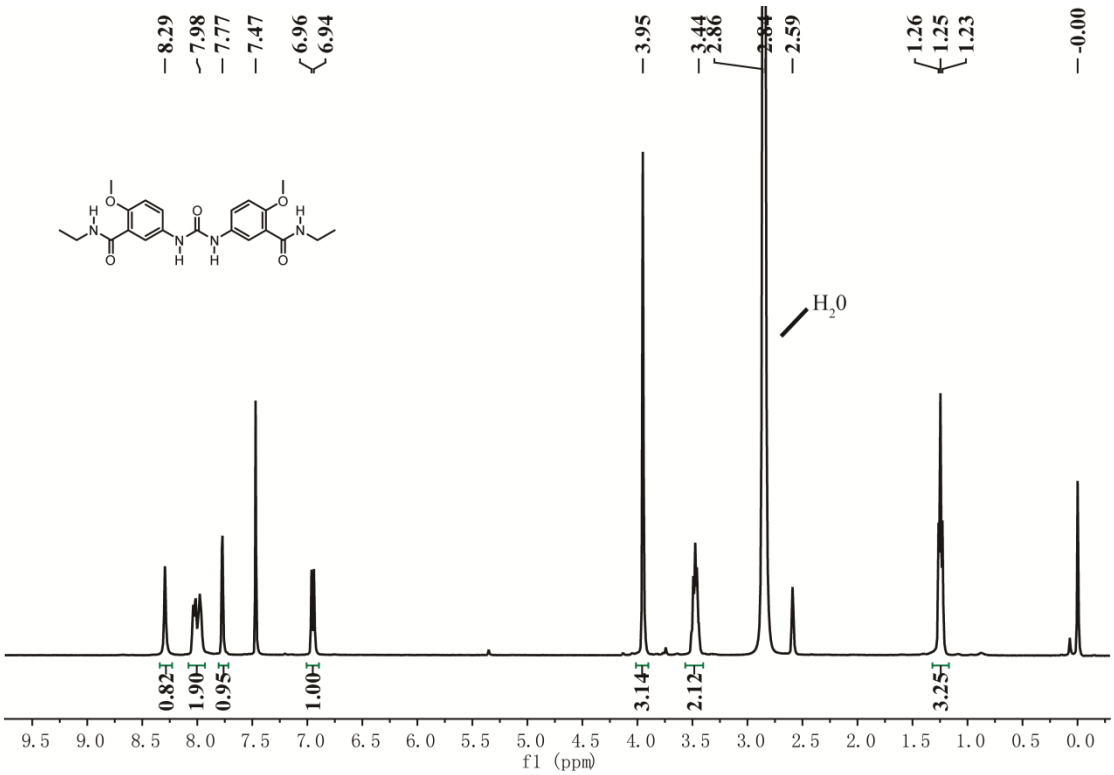


Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$/DMSO-d_6) of **2c**.

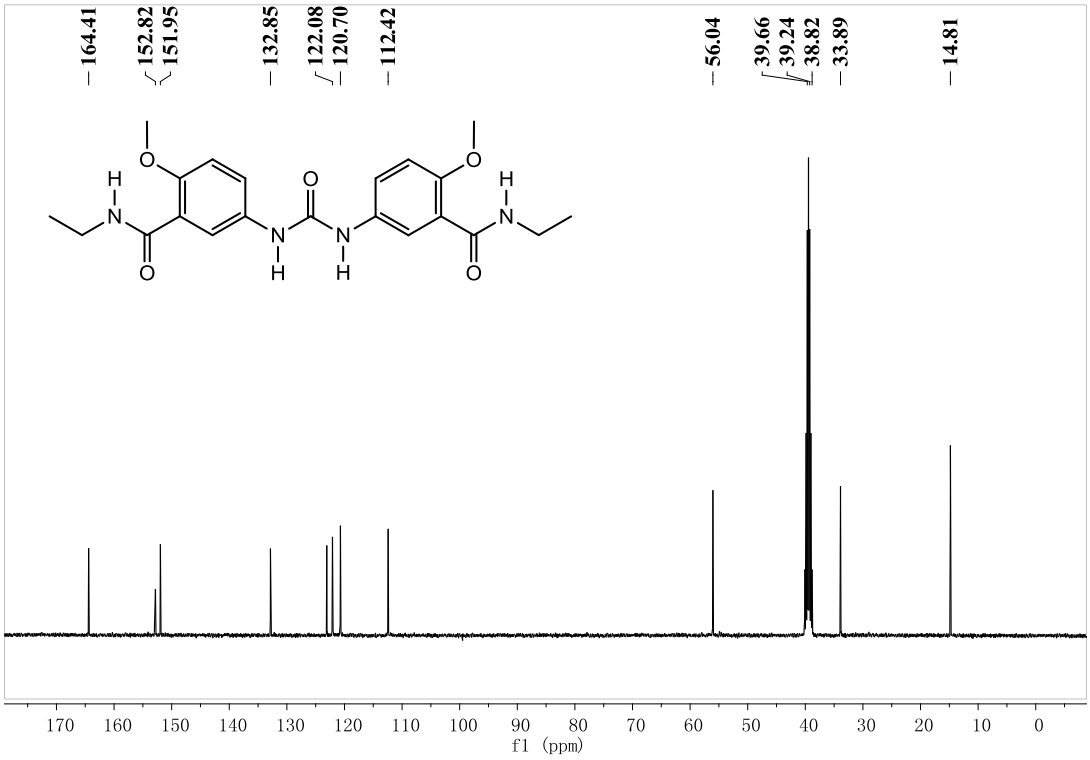


Figure S29. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **2c**.

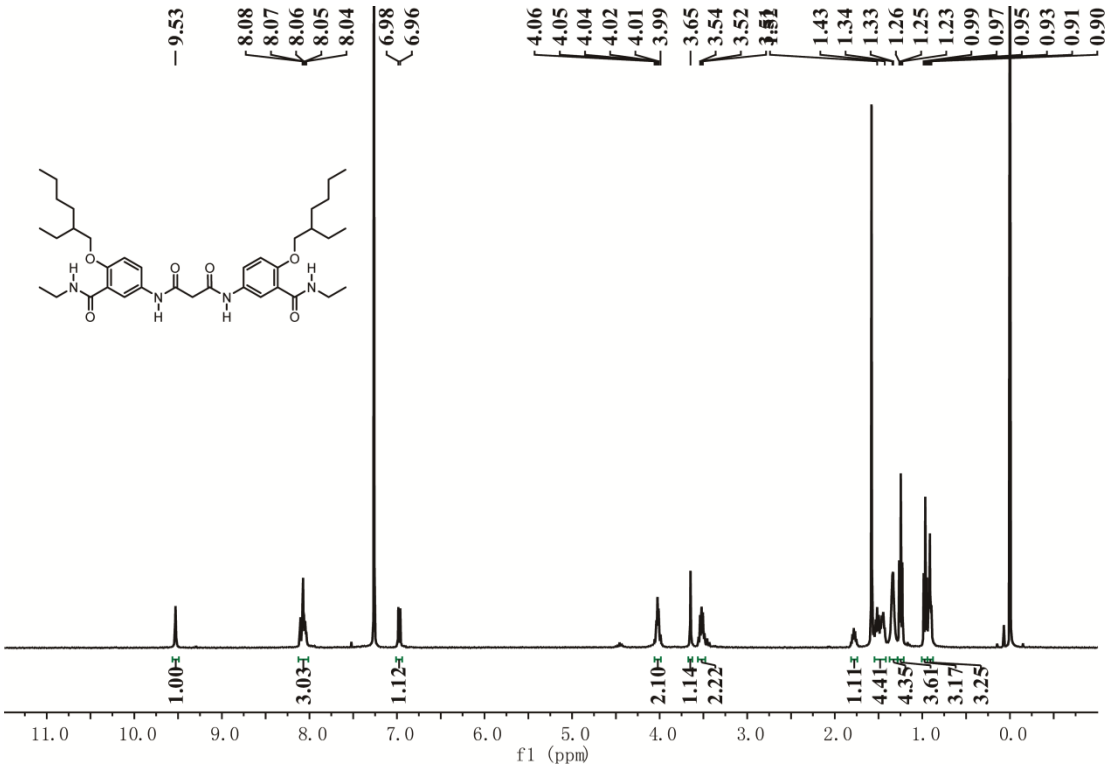


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**.

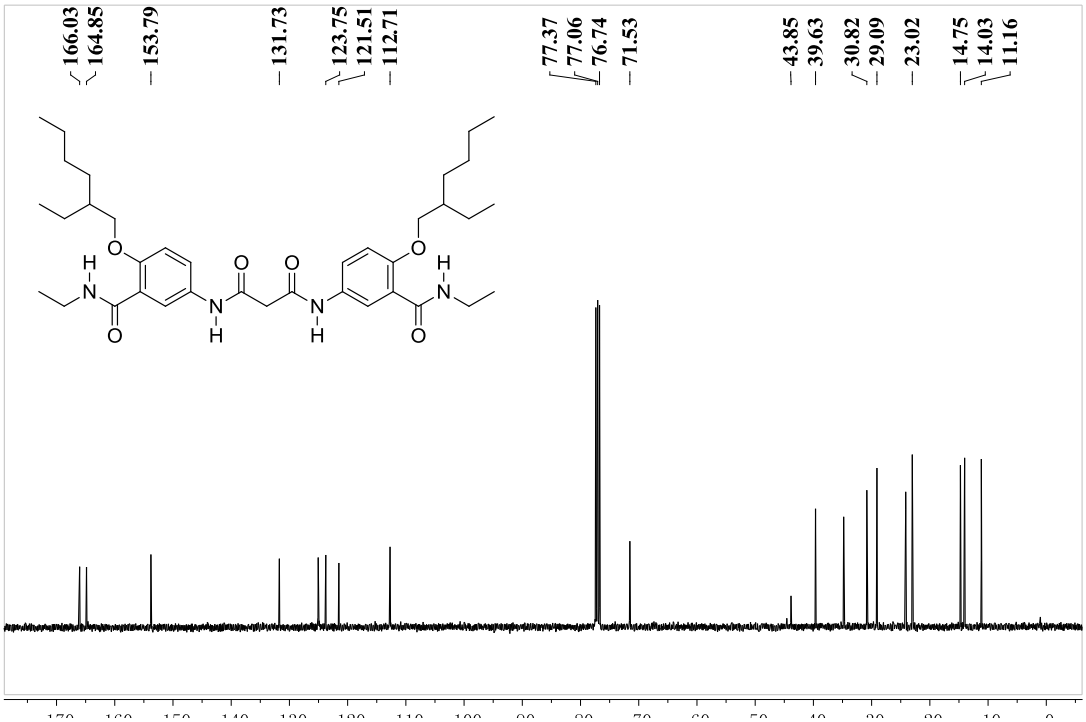


Figure S31. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2d**.

7. References

1 (a) K. A. Connors, *Binding Constants*; Wiley: New York, 1987; (b) P. Thordarson "Binding Constants and Their Measurement" in Supramolecular Chemistry: From Molecules to Nanomaterials, DOI: 10.1002/9780470661345. smc018, Wiley, 2012. (c) A. P. Bisson, F. J. Carver, D. S. Eggleston, R. C. Haltiwanger, C. A. Hunter, D. L. Livingstone, J. F. McCabe, C. Rotger and A. E. Rowan, *J. Am. Chem. Soc.*, 2000, **122**, 8856.

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