

## Tuning luminescence behaviors of a chloroplatinum(II) complex by component exchanges of dynamic acylhydrazone bond

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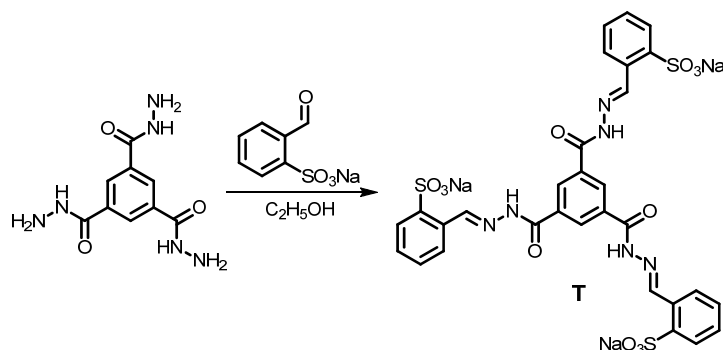
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### Materials and Instruments.

All solvents and reagents were of reagent grade quality and purchased commercially.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz spectrometer, performing in  $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$  or  $d_6$ -DMSO solutions and using TMS as an internal standard. Electrospray ionization mass spectra (ESI-MS) were performed with Bruker microTOF-Q II. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. TEM images were obtained with an FEI Tecnai F30 operating at 300 kV. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Fluorescence microscopy measurements were carried out on a Leica DM4000B. All measurements were carried out at room temperature.

In order to avoid the systematic errors, we used the same measurement conditions: the same concentrations of **Pt-bzimpy** (0.45 mM) and **T** (0.15 mM), the same cells, the same spectrofluorimeter of *Hitachi F-7000*, the same  $\lambda_{\text{ex}}$  at 420 nm, the same gap width of 5 nm, and the measuring temperature at 25 °C. Thus, the initial luminescence intensities of **Pt-bzimpy-T** varied in the allowable error from 2045 to 2068. So, the luminescence varieties of the component exchanges could be compared on the basis of their data.

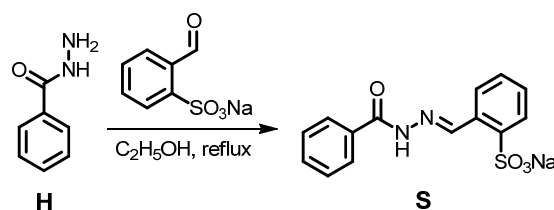
Hexaethylene glycol monomethyl ether iodide,<sup>1</sup> the chloroplatinum(II) complex of 2,6-bis(benzimidazol-2'-yl)pyridine bearing two hexaethylene glycol methyl ether groups (**Pt-bzimpy**)<sup>1</sup> and benzoyl hydrazide<sup>2</sup> were prepared according to the related literatures.



### tripodal hydrazone-linked sodium benzene sulfonate (T)

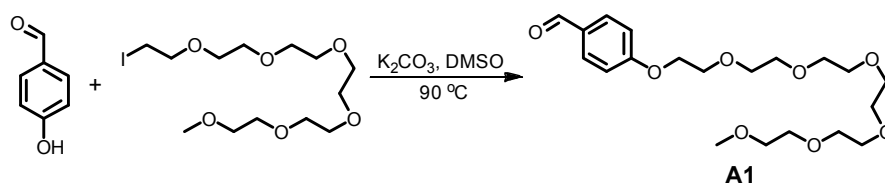
1,3,5-tricarbohydrazine benzene (1 g, 4.0 mmol) was added to a hot solution of 2-formylbenzenesulfonate sodium (2.7 g, 13.2 mmol) in 100 mL ethanol. The resulting mixture was refluxed for 3 d, and then cooled to room temperature. Precipitate was collected via filter and

washed by hot ethanol. Pure compound **T** was obtained as a white solid (2.4 g, 74 % yield). <sup>1</sup>H NMR (δ, ppm, d<sub>6</sub>-DMSO): 7.43 – 7.39 (m, 6H), 7.82 – 7.94 (m, 3H), 8.06 – 8.03 (dd, 3H), 9.41 (s, 3H), 12.47 (s, 3H). <sup>13</sup>C NMR (δ, ppm, d<sub>6</sub>-DMSO): 126.5, 127.4, 129.0, 129.9, 130.9, 131.7, 134.2, 147.4, 149.0, 162.8. HR-ESI-MS: m/z Calcd for [C<sub>30</sub>H<sub>21</sub>N<sub>6</sub>O<sub>12</sub>S<sub>3</sub>]<sup>3-</sup>: 251.0132, found 251.0132, Calcd for [C<sub>30</sub>H<sub>23</sub>N<sub>6</sub>O<sub>12</sub>S<sub>3</sub>]<sup>-</sup>: 755.0542, found 755.0535. Anal. Calcd for C<sub>30</sub>H<sub>21</sub>N<sub>6</sub>O<sub>12</sub>S<sub>3</sub>Na<sub>3</sub>·3H<sub>2</sub>O·C<sub>2</sub>H<sub>5</sub>OH: C 41.65, H 3.60, N 9.11. Found: C 41.53, H 3.56, N 9.16.



### Tripodal hydrazone-linked benzene sulfonate (**S**)

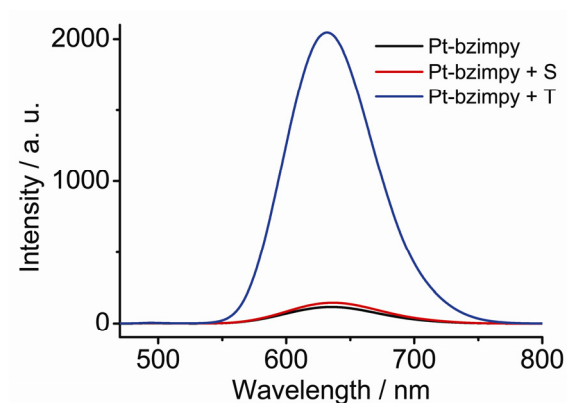
The procedure was similar to that for the preparation of **T**, except benzoyl hydrazide **H** (1.0 g, 7.4 mmol) was used in place of 1,3,5-tricarbohydrazine benzene. 2-formylbenzenesulfonate sodium was adjusted to 2.3 g (11.1 mmol). **S** was obtained as a white solid (1.8 g, 74 % yield). <sup>1</sup>H NMR (δ, ppm, d<sub>6</sub>-DMSO): 7.42 – 7.36 (m, 2H), 7.52 – 7.48 (t, 2H), 7.60 – 7.56 (t, 1H), 7.81 – 7.79 (t, 1H), 8.01 – 7.96 (t, 3H), 9.35 (s, 1H), 12.18 (s, 1H). <sup>13</sup>C NMR (δ, ppm, d<sub>6</sub>-DMSO): 125.8, 126.8, 127.8, 128.3, 128.8, 131.3, 131.6, 133.4, 146.9, 148.0, 163.3. MS (ESI): m/z Calcd for [C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>S]<sup>-</sup> 303.0445, found 303.0449. Anal. Calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>SNa·1.5H<sub>2</sub>O: C 47.59, H 3.99, N 7.93. Found: C 47.33, H 3.91, N 7.96.



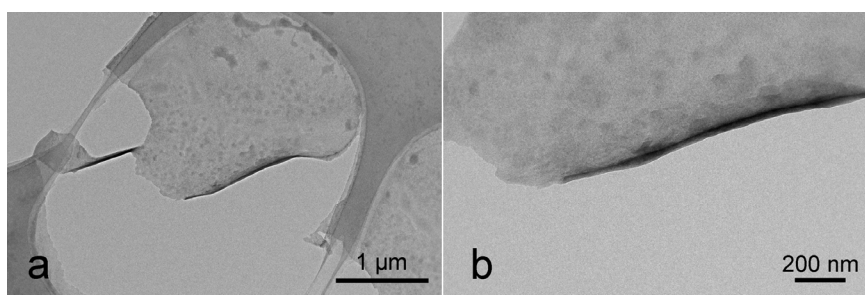
### Benzaldehyde with hexaethylene glycol methyl ether groups (**A1**)

The mixture of 4-hydroxybenzaldehyde (54 mg, 0.44 mmol) and K<sub>2</sub>CO<sub>3</sub> (92 mg, 0.67 mmol) in DMSO (10 mL) was stirred for 0.5 h at 90 °C. Then, a solution of compound **1** (0.2 g, 0.44 mmol) in DMSO (5 mL) was added slowly. The mixture was stirred for another 1 d and cooled to room temperature. After removal of the solvents in vacuo, the residue was redissolved in H<sub>2</sub>O and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated to yield a crude product. Pure compound **A** was obtained as a highly viscous liquid by column chromatography on silica gel (ethyl acetate/ethanol, 4:1, 0.12 g, 67 % yield). <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 3.37 (s, 3H), 3.54 – 3.53 (t, 2H), 3.69 – 3.62 (m, 16H), 3.74 – 3.72 (m, 2H), 3.90 – 3.88 (t, 2H), 4.23 – 4.20 (t, 2H), 7.03 – 7.01 (dd, 2H), 7.84 – 7.82 (dd, 2H), 9.88 (s, 1H). <sup>13</sup>C NMR (δ, ppm, CDCl<sub>3</sub>): 59.2, 68.0, 69.7, 70.8, 71.2, 72.1, 115.1, 130.3, 132.1, 164.1, 191.0. MS (ESI): m/z Calcd for [C<sub>20</sub>H<sub>32</sub>O<sub>8</sub>Na]<sup>-</sup>: 423.1994, found 423.1995. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>O<sub>8</sub>·7H<sub>2</sub>O: C 45.62, H 8.81. Found: C 45.83, H 8.91.

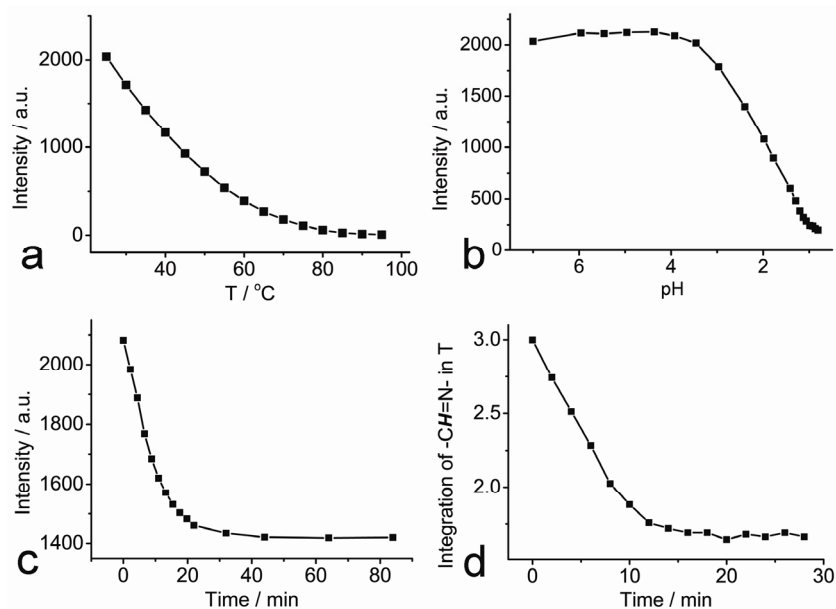
1. J. Liang, X. Zheng, L. He, H. Huang and W. Bu, *Dalton Trans.*, 2014, **43**, 13174.
2. L. Y. Zhao, Q. L. Mi, G. K. Wang, J. H. Chen, J. F. Zhang, Q. H. Zhao, Y. Zhou, *Tetrahedron Lett.*, 2013, **54**, 3353.



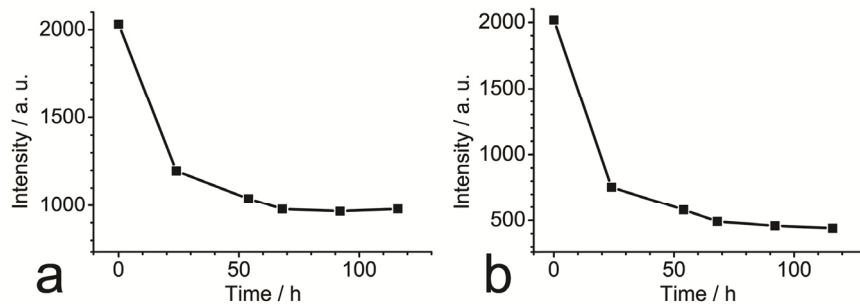
**Fig. S1** Emission spectra of **Pt-bzimpy** (0.45 mM), **Pt-bzimpy + S** (**Pt-bzimpy**, 0.45 mM and **S**, 0.45 mM), and **Pt-bzimpy + T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM).



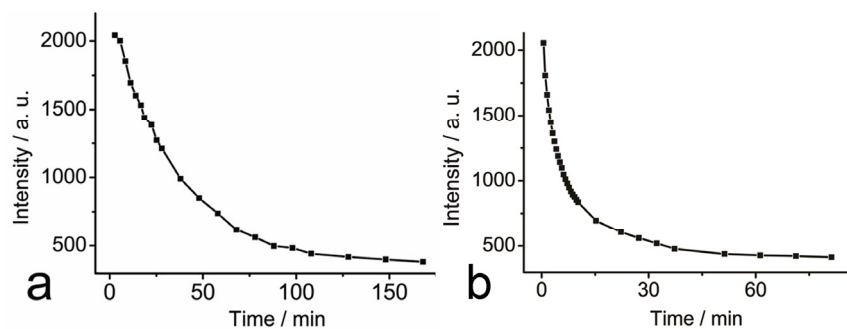
**Fig. S2** TEM images of **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM).



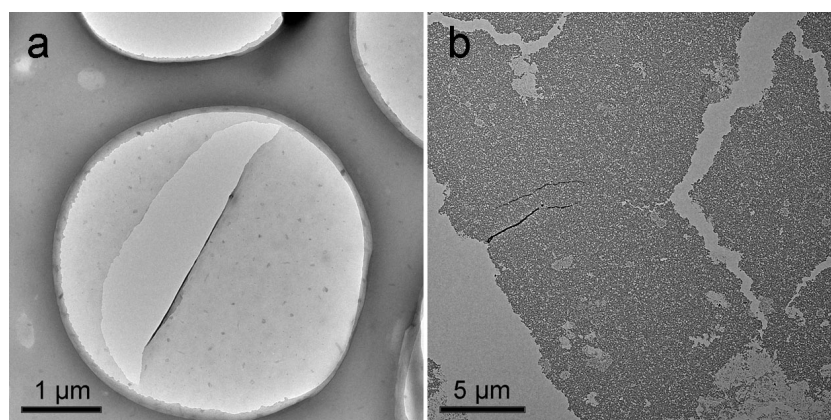
**Fig. S3** Plots of emission at 632 nm for **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM), versus (a) increasing temperature and (b) pH Changes. Plots of (c) emission for **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM) and (d) integration of imine hydrogen of **T** (4 mM, in  $D_2O$ ) in  $^1H$  NMR spectra versus time at pH 2.



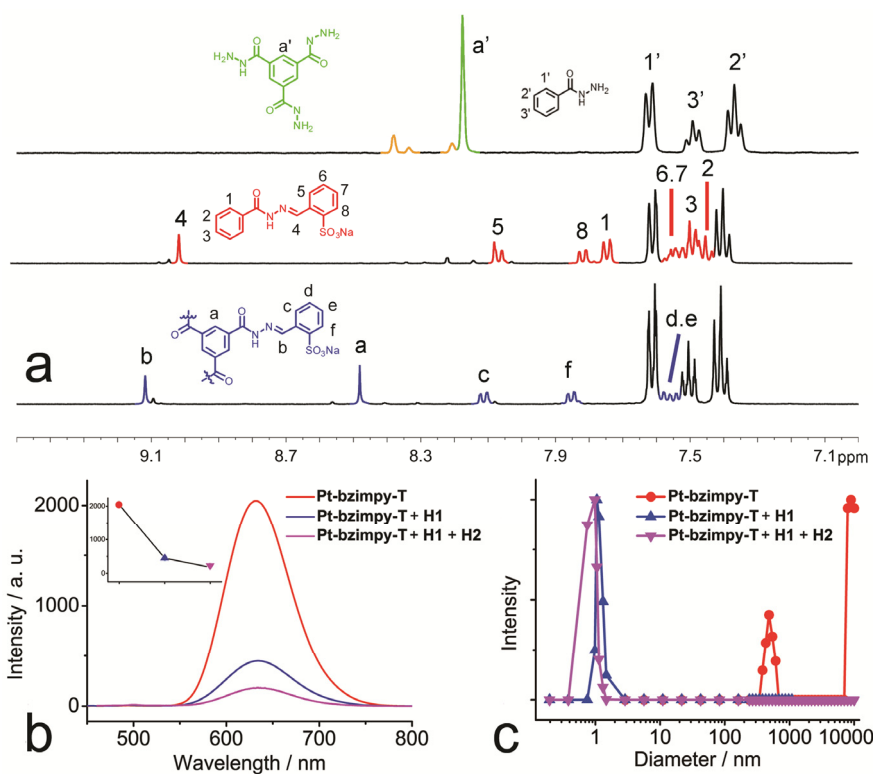
**Fig. S4** Time-dependent emission intensities of **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM) upon the additions of (a) 9 equiv **A1** and (b) **H1** per **T** at pH 4, respectively.



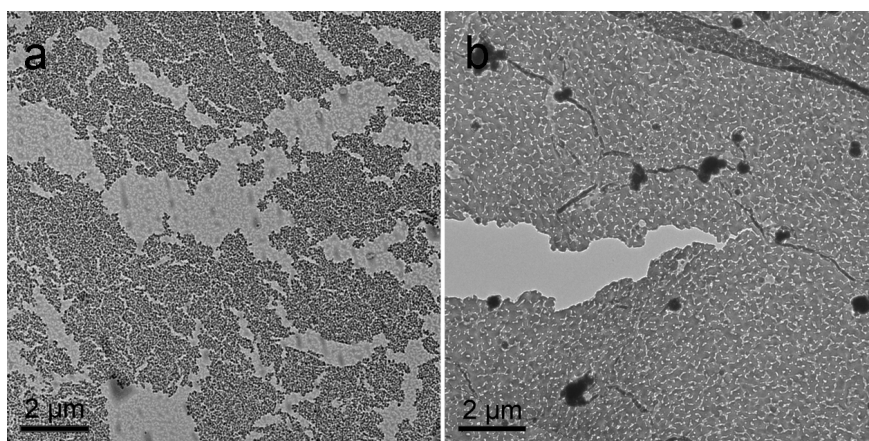
**Fig. S5** Time-dependent emission intensities of **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM) upon the additions of (a) 9 equiv **A1** and (b) **H1** per **T** at pH 2, respectively.



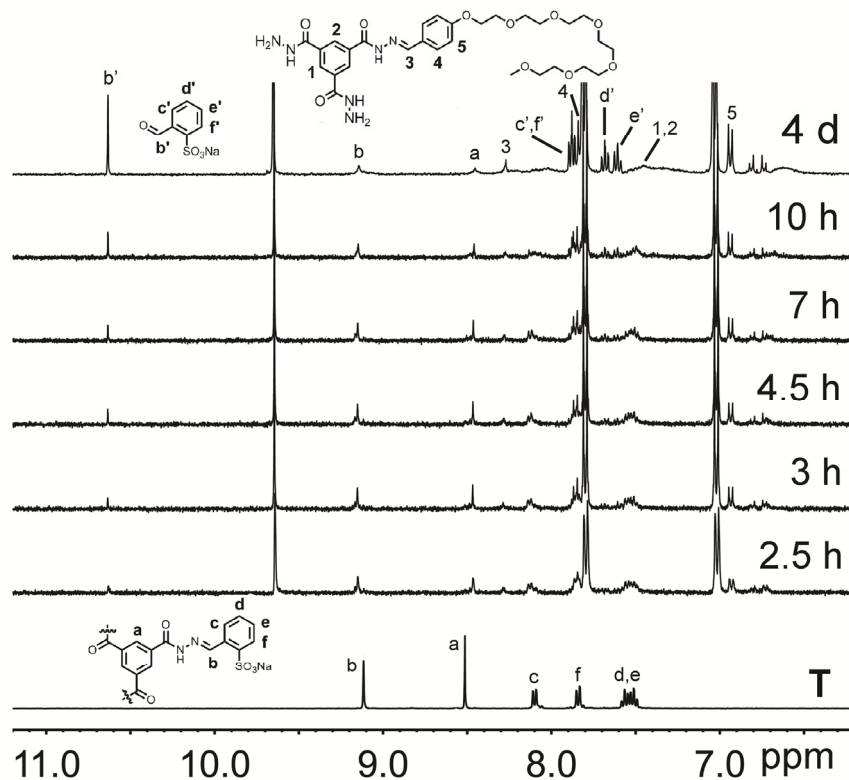
**Fig. S6** TEM images of aldehyde exchanges upon successive additions of (a) 9 equiv **A1** and (b) 81 equiv **A2** per **T** to **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM) at pH 4.



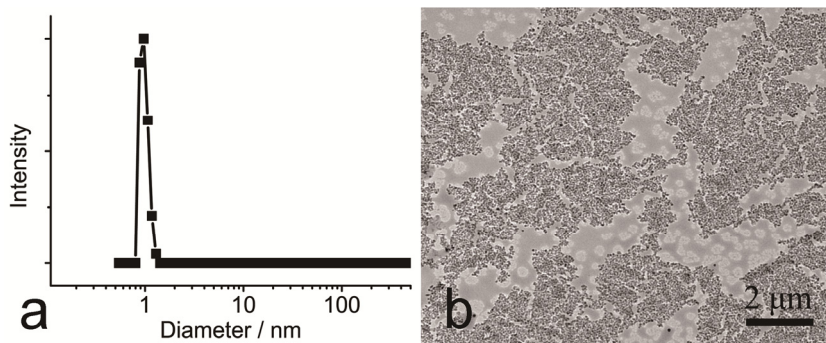
**Fig. S7** (a)  $^1\text{H}$  NMR profiles of twice hydrazine exchanges upon additions of 9 equiv **H1** and 81 equiv **H2** to **T** (4 mM) at pH 4. (b) Luminescence and (c) DLS plots of twice hydrazine exchanges upon additions of 9 equiv **H1** and 81 equiv **H2** per **T** to **Pt-bzimpy-T** (**Pt-bzimpy**, 0.45 mM and **T**, 0.15 mM) at pH 4.



**Fig. S8** TEM images of hydrazine exchanges upon successive additions of (a) 9 equiv **H1** and (b) 81 equiv **H2** per **T** to **Pt-bzimpy-T** (0.15 mM) at pH 4



**Fig. S9**  $^1\text{H}$  NMR spectra of component exchanges upon addition of 9 equiv **A1** to **T** (4 mM) at pH 4. From bottom to top: pure **T**, **T** + **A1** at 2.5 h, 3h, 4.5 h, 7 h, 10 h, and 4 d.



**Fig. S10** (a) DLS and (b) TEM plots of **Pt-bzimpy** (0.45 mM) upon addition of 1 equiv **S**.

**Table S1** The constants in the nonlinear relationship of emission intensities ( $\gamma$ ) at 632 nm versus the molar ratios ( $x$ ) of **A1/T** or **H1/T**.

	a	b	c	d
aldehyde exchange	626	$6.36 \times 10^5$	0.185	6.16
hydrazine exchange	456	7309	0.535	1.214