**Supporting Information**

# Fluorescent sensor array for separation-free dopamine analogue discrimination via polyethyleneimine-mediated self-polymerization reaction

Ye Sun,[a] Fengniu Lu,[b]Hongwei Yang,[a] Caifeng Ding,[c] Zhiqin Yuan,*[a] and Chao Lu *[a]

a. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

b. Frontier Molecules Group, International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan.

c. Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, Ministry of Education; Qingdao University of Science and Technology, Qingdao 266042, China

E-mail: yuanzq@mail.buct.edu.cn (Z. Yuan)

E-mail: luchao@mail.buct.edu.cn (C. Lu)

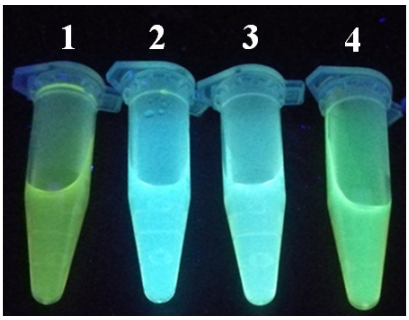


**Fig. S1** Photographs of hPEI-DA analogue mixture solution after 35 min reaction at 50 ˚C. From 1 to 4: hPEI-DA mixture, hPEI-DOPA mixture, hPEI-DOPAM mixture, and hPEI-LNAA mixture, respectively.

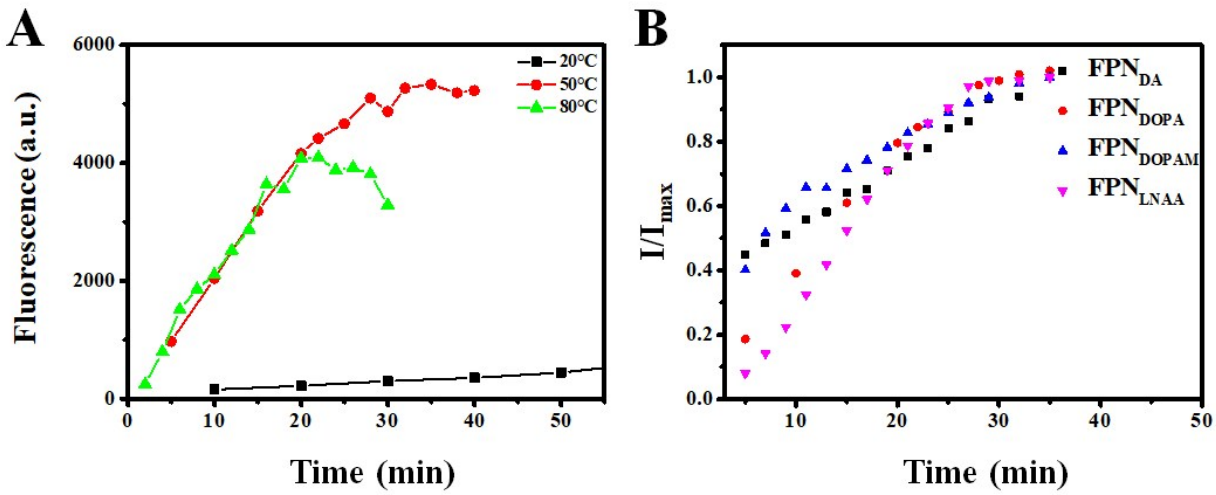


**Fig. S2** Plots of time-dependent fluorescence of LNAA-hPEI mixture under various reaction temperatures (A). Time-dependent relative fluorescence intensity variations of four FPNs at 50 ˚C condition (B). The total concentrations of DA analogues are 1.0 μM.

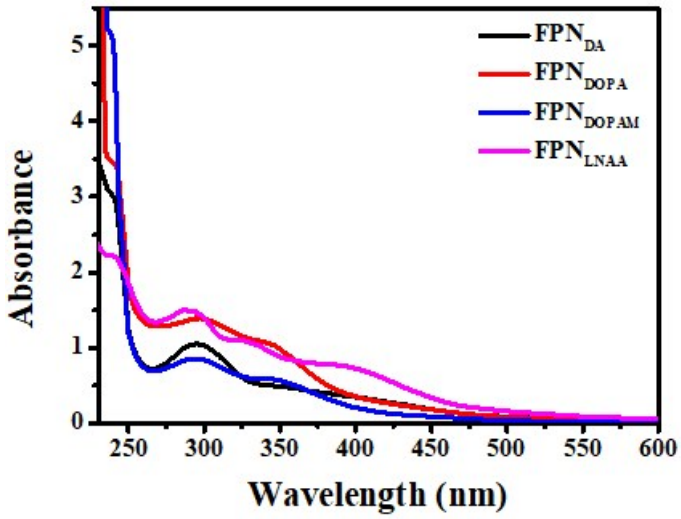


**Fig. S3** Absorption spectra of $FPN_{DA}$ (black line), $FPN_{DOPA}$ (red line), $FPN_{DOPAM}$ (blue line) and $FPN_{LNAA}$ (purple line).

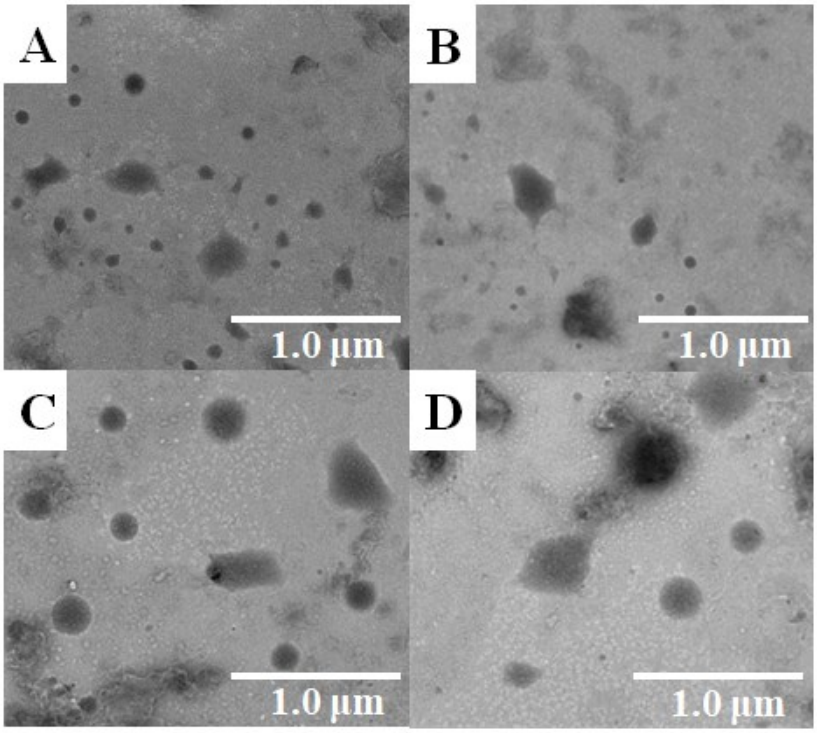


**Fig. S4** TEM images of $FPN_{DA}$ (A), $FPN_{DOPA}$ (B), $FPN_{DOPAM}$ (C) and $FPN_{LNAA}$ (D).

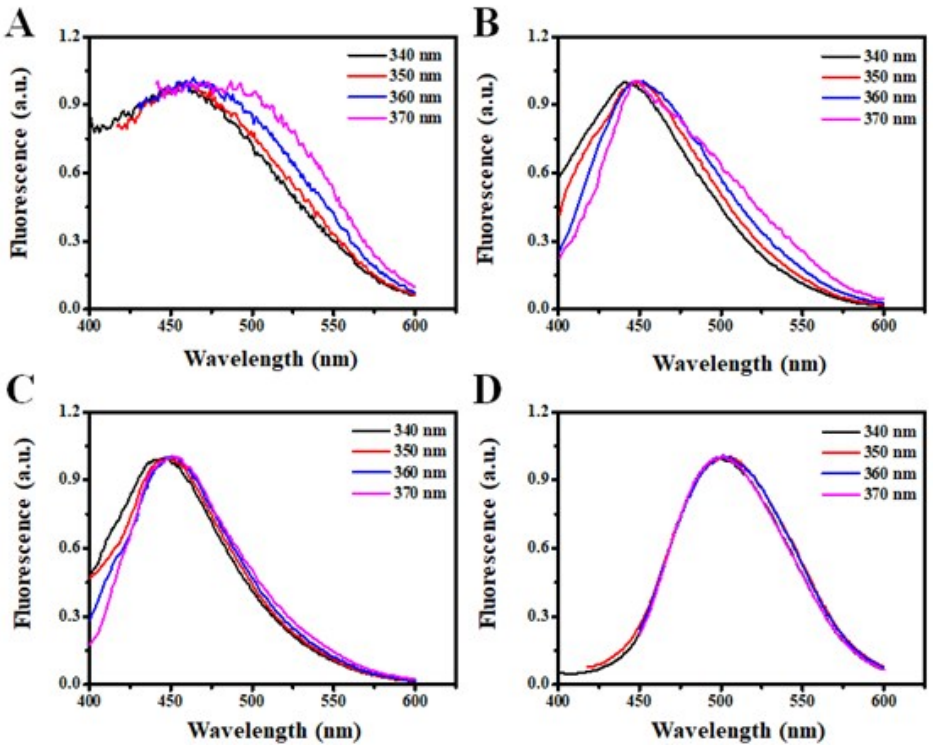


**Fig. S5** Normalized fluorescence emission spectra of $FPN_{DA}$ (A), $FPN_{DOPA}$ (B), $FPN_{DOPAM}$ (C), and $FPN_{LNAA}$ (D) under various excitation wavelengths. The total concentrations of DA analogues are 1.0 μM.

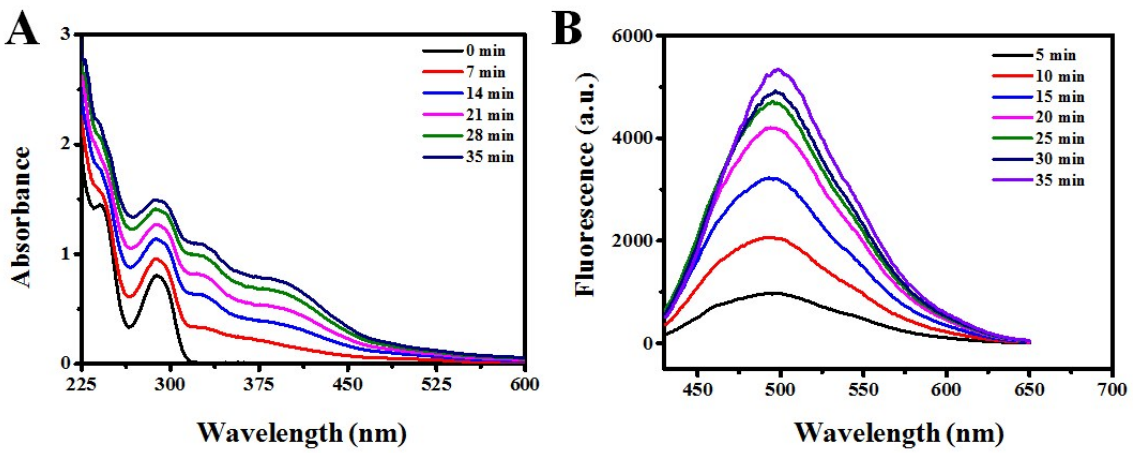


**Fig. S6** Time-dependent absorption (A) and fluorescence emission (B) spectra of hPEI-LNAA mixture at 50 ˚C condition.

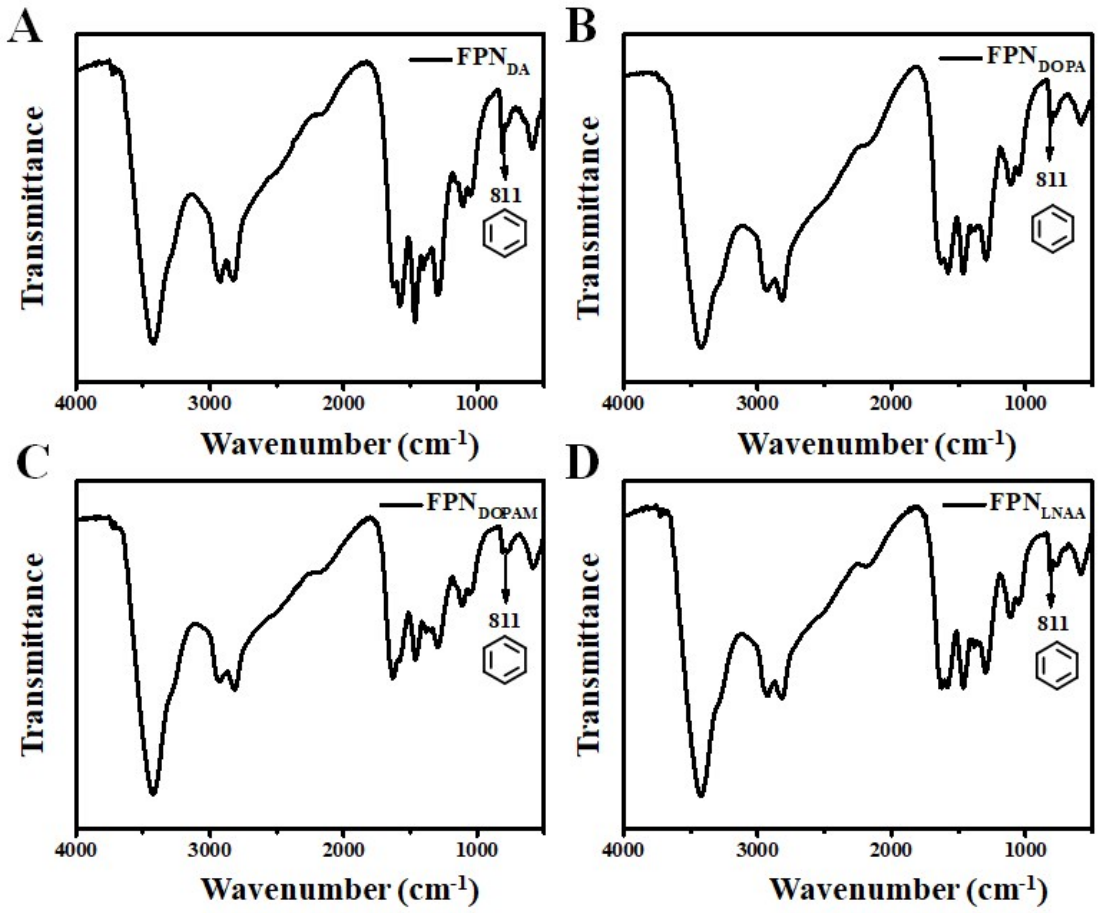


**Fig. S7** FT-IR spectra of $FPN_{DA}$ (A), $FPN_{DOPA}$ (B), $FPN_{DOPAM}$ (C) and $FPN_{LNAA}$ (D).

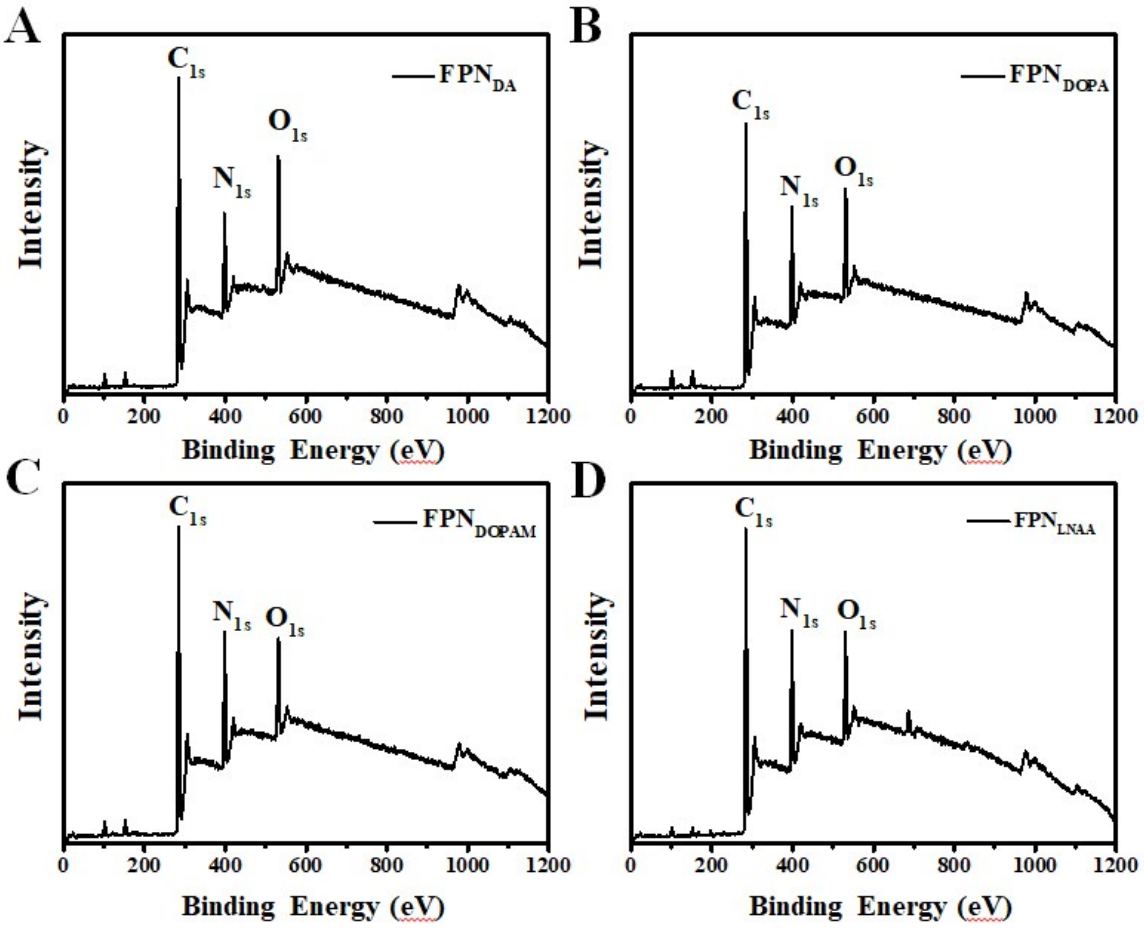


**Fig. S8** XPS spectra of $FPN_{DA}$ (A), $FPN_{DOPA}$ (B), $FPN_{DOPAM}$ (C) and $FPN_{LNAA}$ (D).

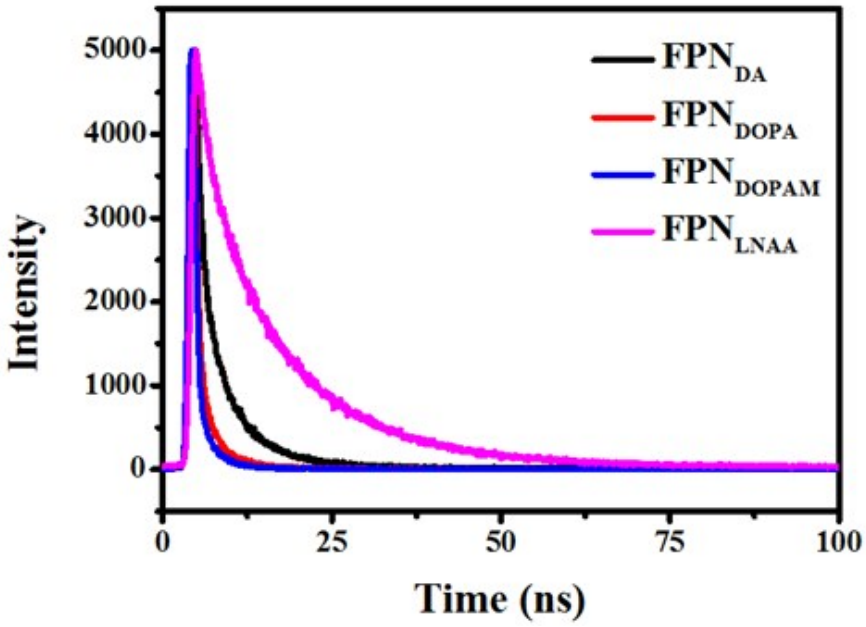


**Fig. S9** Time-resolved fluorescence emission spectra of $FPN_{DA}$ (black line), $FPN_{DOPA}$ (red line), $FPN_{DOPAM}$ (blue line) and $FPN_{LNAA}$ (purple line).

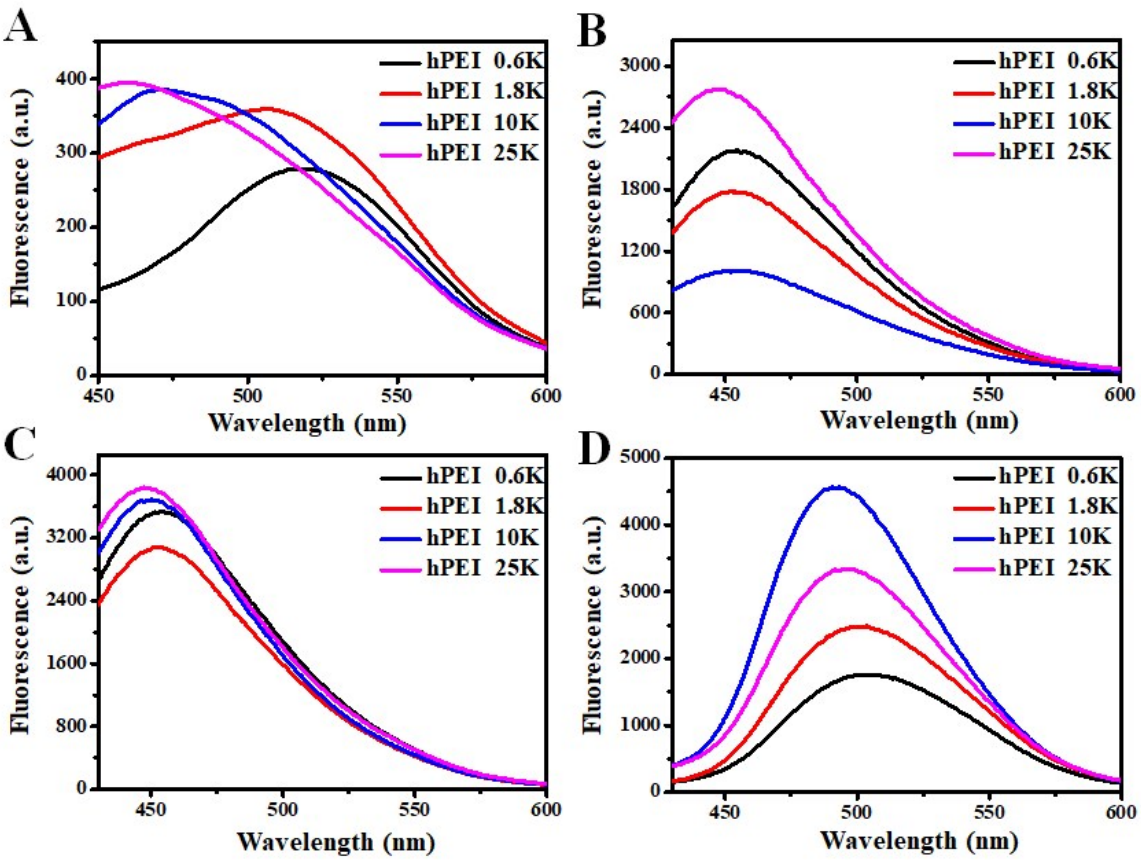


**Fig. S10** Fluorescence emission spectra of resulted $FPN_{DA}$ (A), $FPN_{DOPA}$ (B), $FPN_{DOPAM}$ (C) and $FPN_{LNAA}$ (D) upon addition of four hPEIs with different molecular weights.

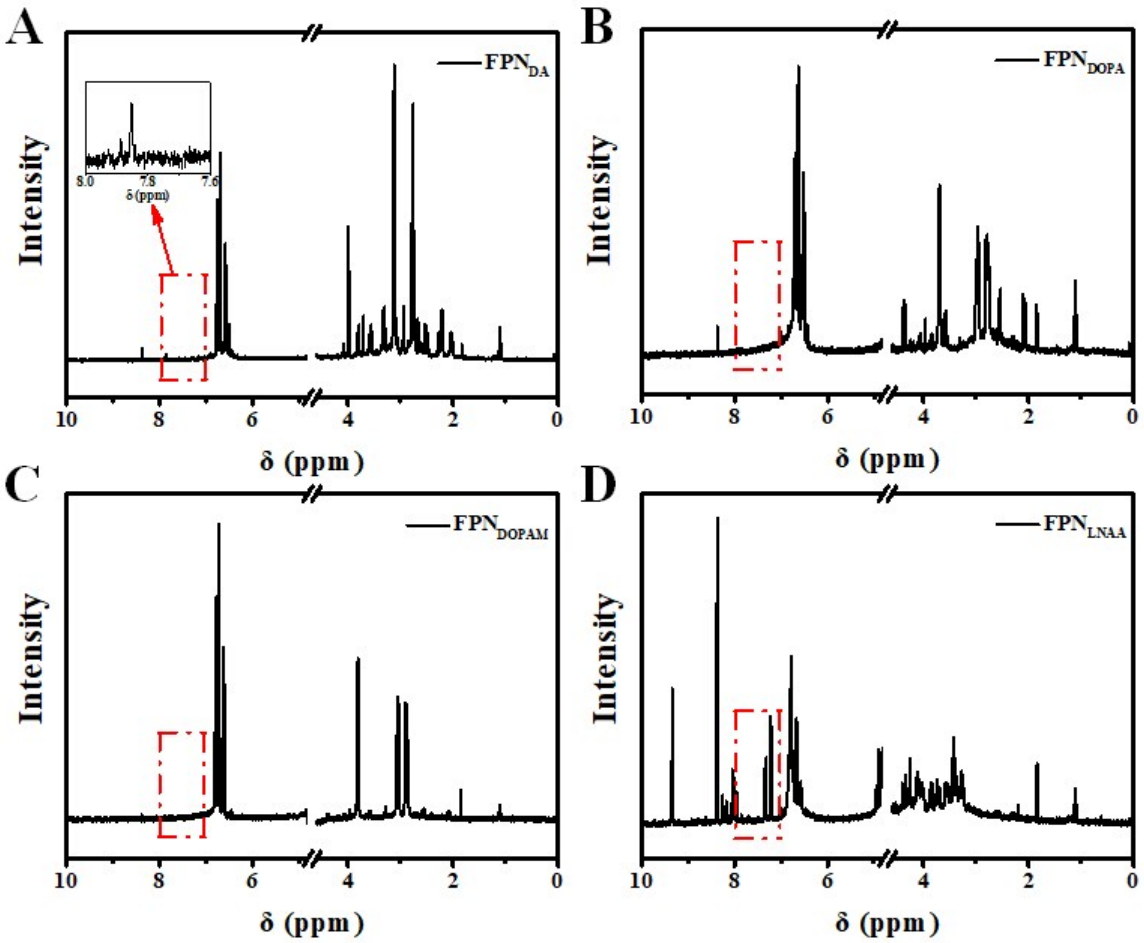


**Fig. S11** $^{1}$H NMR spectra of four FPNs, from A to D: $FPN_{DA}$, $FPN_{DOPA}$, $FPN_{DOPAM}$, and $FPN_{LNAA}$, respectively. The molecular weight of hPEI is 10 KDa.

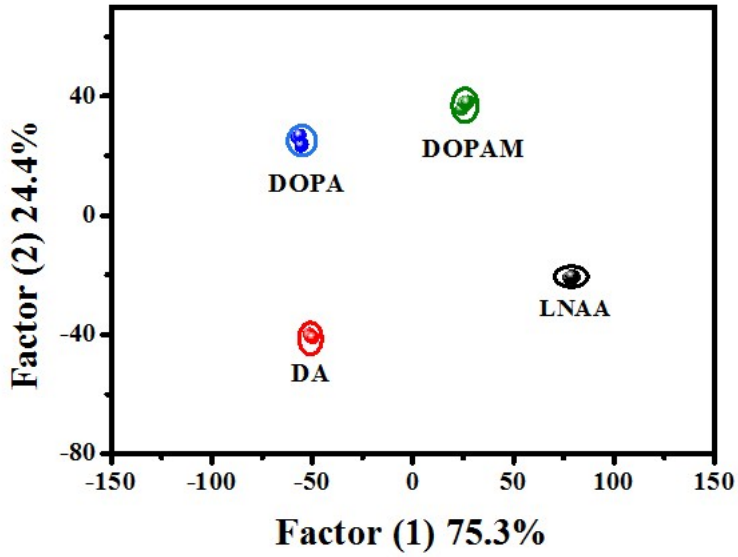


**Fig. S12** Canonical score plots for the first two factors of relative fluorescence increase $(I - I_{ref})/I_{ref}$ patterns from four DA analogues analyzed by LDA. The total concentrations of DA analogues are 1.0 μM.

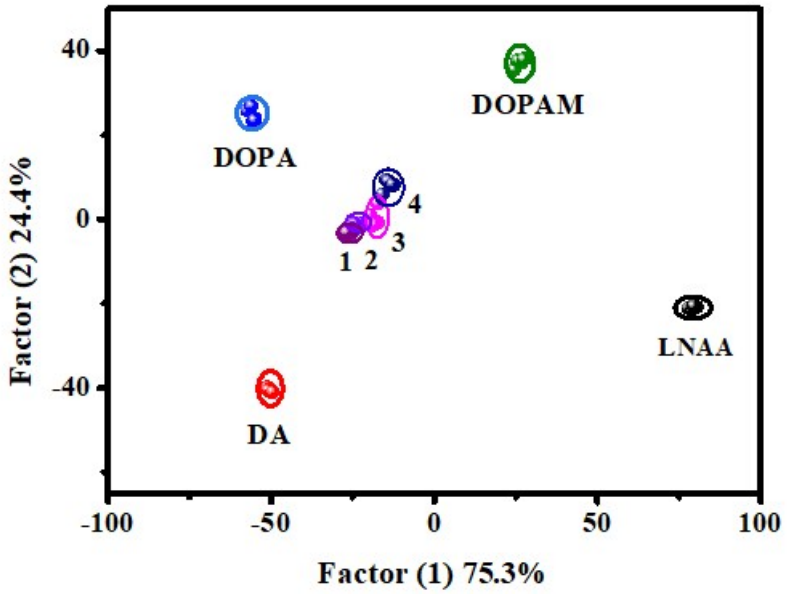


**Fig. S13** Canonical score plots for the first two factors of relative fluorescence increase $(I - I_{ref})/I_{ref}$ and emission maximum increase $(\lambda_{max} - \lambda_{ref})/48$ patterns from four DA analogues (1.0 μM) and potential interferents (1.0 μM) analyzed by LDA. Compounds 1 to 4 represent catechin, tannic acid, catechol, and 3,4-dihydroxybenzoic acid, respectively. The total concentrations of DA analogus or interferents are 1.0 μM.

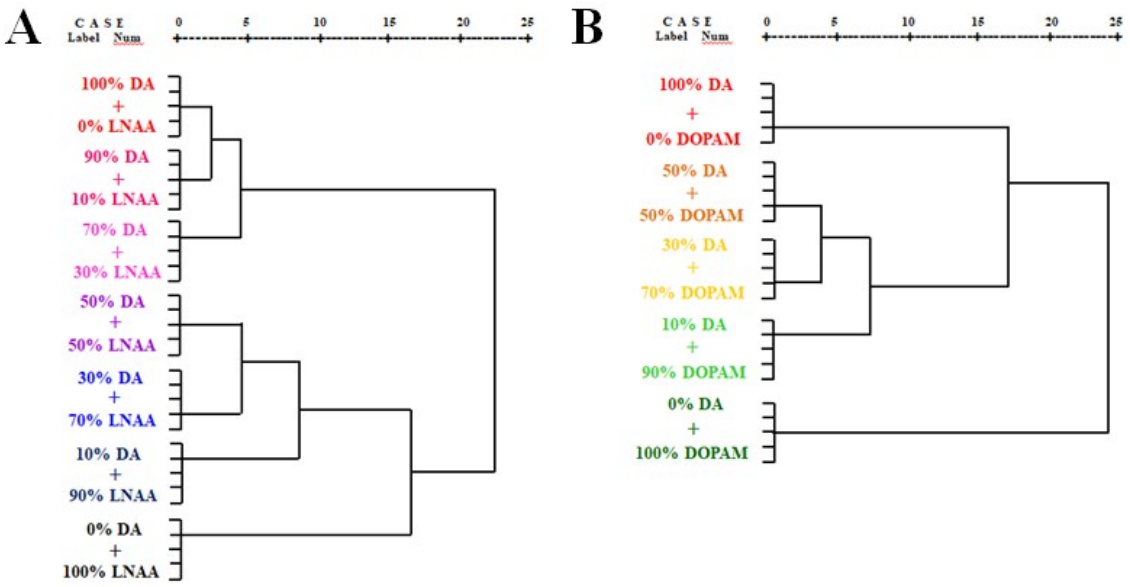


**Fig. S14** HCA analysis of DA/DOPAM mixture (A) and DA/LNAA mixture (B) samples with five parallel measurements.

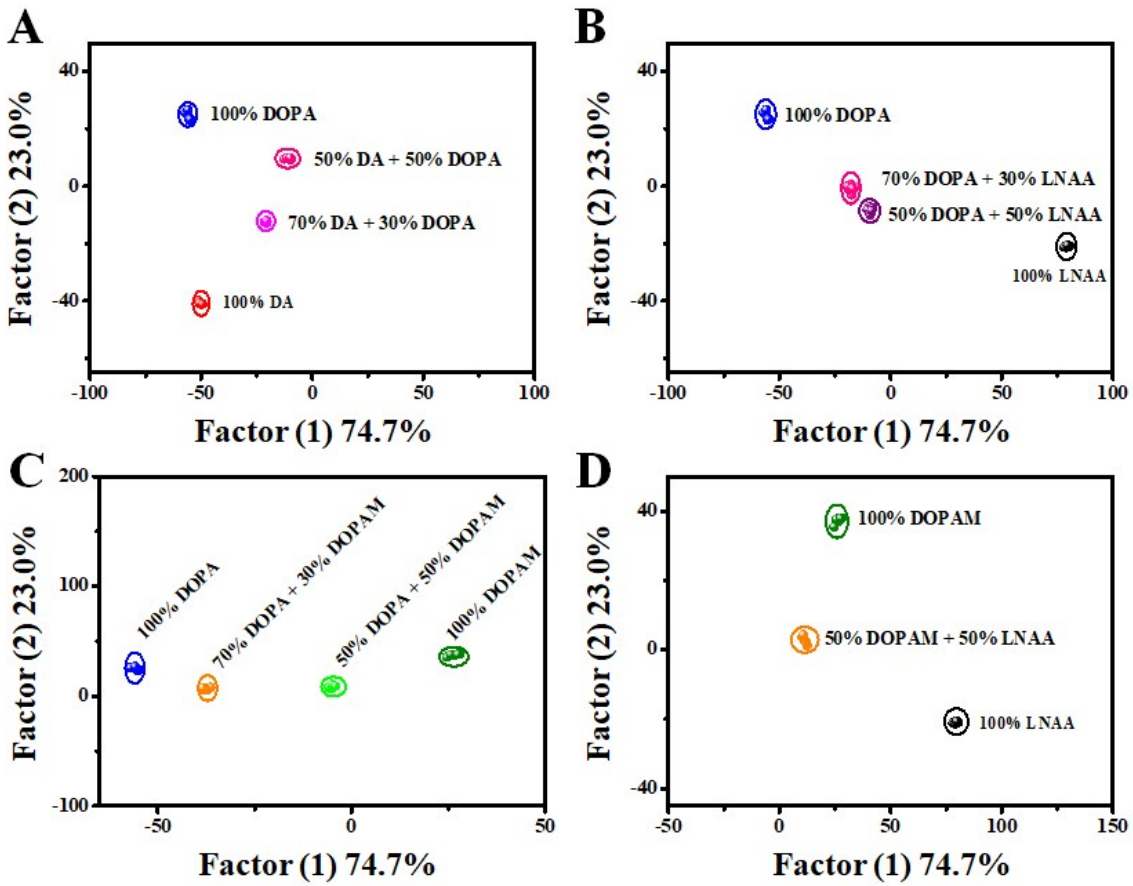


**Fig. S15** Canonical score plots for the first two factors of relative fluorescence increase $(I - I_{ref})/I_{ref}$ and emission maximum increase $(\lambda_{max} - \lambda_{ref})/48$ patterns from binary dopamine analogues by DA/DOPA mixture (A), DOPA/LNAA mixture (B), DOPA/DOPAM mixture (C), and DOPAM/LNAA mixture (D). The total concentrations of DA analogues are 1.0 μM.

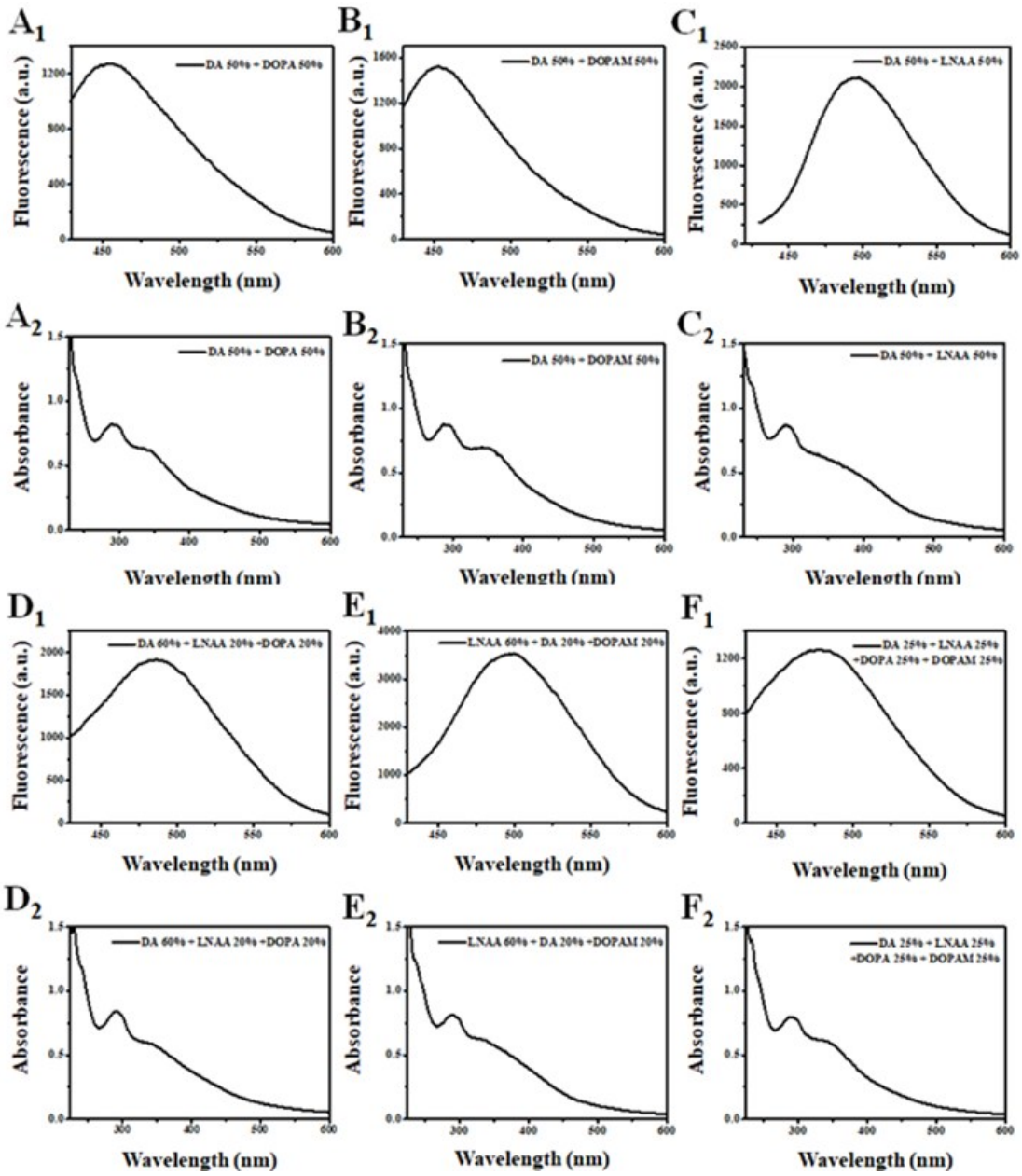


**Fig. S16** Fluorescence emission (1) and UV-vis absorption (2) spectra of the products from the reactions of hPEI (10 KDa) and mixed DA analogues. A to F represent binary, tertiary and quarternary mixtures of DA analogues: 50% DA + 50% DOPA (A), 50% DA + 50% DOPAM (B), 50% DA + 50% LNAA (C), 60% DA + 20% LNAA + 20% DOPA (D), 60% LNAA + 20% DA +DOPA 20% (E), and 25% DA + 25% LNAA + 25% DOPA + 25% DOPAM (F), respectively. The total concentrations of DA analogues are 1.0 μM.

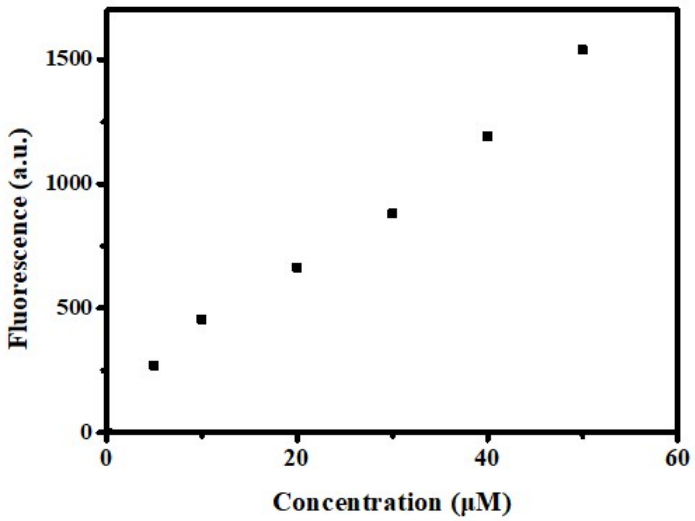


**Fig. S17** Plots of fluorescence intensity of $FPN_{DA}$ *versus* DA concentration in diluted fetal bovine serum.

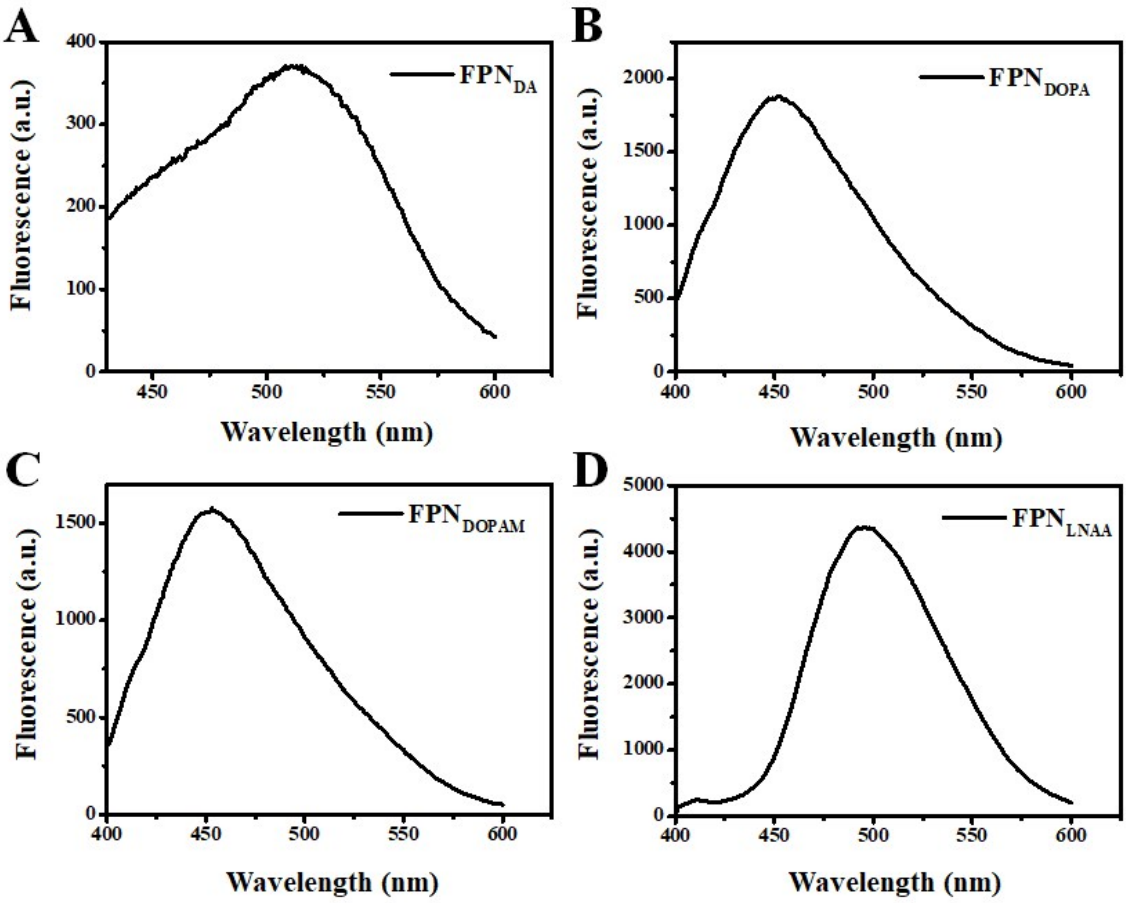


**Fig. S18** Fluorescence emission spectra of formed FPNs in fetal bovine serum, from A to D: $FPN_{DA}$, $FPN_{DOPA}$, $FPN_{DOPAM}$, and $FPN_{LNAA}$, respectively. The concentrations of DA analogues are 10 μM.

**Table S1**. Identification of 43 unknown sole analogue and 45 unknown analogues mixture samples.

| # | $(I-I_{ref})/I_{ref}$ | | | | $(\lambda_{max}-\lambda_{ref})/48$ | | | | Identi. | Verifi. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0.6 KDa | 1.8 KDa | 10 KDa | 25 KDa | 0.6 KDa | 1.8 KDa | 10 KDa | 25 KDa | | |
| 1 | 0.4846 | -0.2720 | -0.3456 | 0.8566 | -0.5256 | -0.5590 | -0.5367 | -0.6217 | DOPA | DOPA |
| 2 | -0.8474 | -0.8391 | -0.6966 | -0.7356 | 0.8235 | 0.5944 | -0.1348 | -0.3848 | DA | DA |
| 3 | 0.1686 | 0.6740 | 2.120 | -0.4639 | 0.4848 | 0.4352 | 0.2531 | 0.3196 | LNAA | LNAA |
| 4 | 0.3966 | 0.1920 | -0.3106 | 1.0260 | -0.5279 | -0.5608 | -0.5479 | -0.6113 | DOPA | DOPA |
| 5 | 0.4186 | 0.2946 | -0.2846 | 0.9173 | -0.5240 | -0.5577 | -0.5531 | -0.6073 | DOPA | DOPA |
| 6 | 1.3640 | 1.1920 | 1.5160 | 1.2920 | -0.5746 | -0.5360 | -0.6131 | -0.6688 | DOPAM | DOPAM |
| 7 | 0.1800 | 0.6853 | 2.0920 | -0.4523 | 0.4808 | 0.4183 | 0.2573 | 0.3198 | LNAA | LNAA |
| 8 | -0.8826 | -0.8432 | -0.7142 | -0.7363 | 0.8023 | 0.5731 | -0.1560 | -0.4060 | DA | DA |
| 9 | 0.3920 | 0.2586 | -0.3300 | 1.018 | -0.5321 | -0.5504 | -0.5400 | -0.6154 | DOPA | DOPA |
| 10 | 0.3693 | 0.2746 | -0.3173 | 0.7013 | -0.5296 | -0.5560 | -0.5433 | -0.6129 | DOPA | DOPA |
| 11 | -0.8860 | -0.8330 | -0.7210 | -0.7219 | 0.8427 | 0.6135 | -0.1156 | -0.3656 | DA | DA |
| 12 | 1.4520 | 1.1820 | 1.5080 | 1.1870 | -0.5621 | -0.5413 | -0.6038 | -0.6663 | DOPAM | DOPAM |
| 13 | 1.4590 | 1.1060 | 1.5000 | 1.2340 | -0.5629 | -0.5421 | -0.6046 | -0.6671 | DOPAM | DOPAM |
| 14 | 0.2373 | 0.6700 | 2.107 | -0.4684 | 0.4788 | 0.4163 | 0.2496 | 0.3121 | LNAA | LNAA |
| 15 | -0.8852 | -0.8407 | -0.6843 | -0.7392 | 0.8287 | 0.5996 | -0.1296 | -0.3796 | DA | DA |
| 16 | 0.3933 | 0.2060 | -0.3200 | 0.6726 | -0.5352 | -0.5592 | -0.5398 | -0.6185 | DOPA | DOPA |
| 17 | 0.1953 | 0.6900 | 2.0520 | -0.4400 | 0.4860 | 0.4235 | 0.2569 | 0.3194 | LNAA | LNAA |
| 18 | 1.3440 | 1.1620 | 1.5660 | 1.290 | -0.5731 | -0.5523 | -0.6148 | -0.6773 | DOPAM | DOPAM |
| 19 | -0.8844 | -0.8441 | -0.6830 | -0.7419 | 0.8094 | 0.5802 | -0.1490 | -0.3990 | DA | DA |
| 20 | 0.2726 | 0.6513 | 2.068 | -0.4687 | 0.4935 | 0.4310 | 0.2644 | 0.3269 | LNAA | LNAA |
| 21 | 1.3890 | 1.1100 | 1.4420 | 1.2440 | -0.5608 | -0.5400 | -0.6025 | -0.6650 | DOPAM | DOPAM |
| 22 | 1.4240 | 1.0390 | 1.5460 | 1.2510 | -0.5765 | -0.5556 | -0.6181 | -0.6806 | DOPAM | DOPAM |
| 23 | -0.8882 | -0.8508 | -0.7166 | -0.7248 | 0.7952 | 0.5660 | -0.1631 | -0.4131 | DA | DA |
| 24 | 0.4066 | 0.1846 | -0.3213 | 0.9340 | -0.5352 | -0.5592 | -0.5398 | -0.6185 | DOPA | DOPA |
| 25 | 1.5080 | 1.0080 | 1.4380 | 1.3090 | -0.5669 | -0.5460 | -0.6085 | -0.6710 | DOPAM | DOPAM |
| 26 | -0.8918 | -0.8446 | -0.7094 | -0.7338 | 0.8283 | 0.5992 | -0.1300 | -0.3800 | DA | DA |
| 27 | -0.8890 | -0.8459 | -0.6847 | -0.7343 | 0.8165 | 0.5873 | -0.1419 | -0.3919 | DA | DA |
| 28 | 0.1693 | 0.6733 | 2.0410 | -0.4458 | 0.4954 | 0.4329 | 0.2662 | 0.3287 | LNAA | LNAA |
| 29 | 0.2000 | 0.6800 | 2.1160 | -0.4476 | 0.4904 | 0.4279 | 0.2613 | 0.3238 | LNAA | LNAA |
| 30 | 1.3930 | 1.1280 | 1.3660 | 1.2150 | -0.5650 | -0.5442 | -0.6067 | -0.6692 | DOPAM | DOPAM |
| 31 | 0.3666 | 0.2426 | -0.3372 | 1.0560 | -0.5383 | -0.5454 | -0.5379 | -0.6217 | DOPA | DOPA |
| 32 | -0.8852 | -0.8407 | -0.6843 | -0.7392 | 0.8056 | 0.5765 | -0.1527 | -0.4027 | DA | DA |
| 33 | 1.2960 | 1.0790 | 1.3550 | 1.1860 | -0.5706 | -0.5498 | -0.6123 | -0.6748 | DOPAM | DOPAM |
| 34 | 0.2220 | 0.6520 | 2.1200 | -0.4606 | 0.4971 | 0.4346 | 0.2679 | 0.3304 | LNAA | LNAA |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 35 | -0.8822 | -0.8426 | -0.7143 | -0.7250 | 0.7477 | 0.5185 | -0.2106 | -0.4606 | DA | DA |
| 36 | 0.4040 | 0.2153 | -0.3146 | 0.9406 | -0.5246 | -0.5510 | -0.5433 | -0.6079 | DOPA | DOPA |
| 37 | 0.2500 | 0.6720 | 2.0770 | -0.4298 | 0.4952 | 0.4327 | 0.2660 | 0.3285 | LNAA | LNAA |
| 38 | 1.4280 | 1.1370 | 1.5360 | 1.2520 | -0.5592 | -0.5383 | -0.6008 | -0.6633 | DOPAM | DOPAM |
| 39 | -0.8876 | -0.8483 | -0.7154 | -0.7236 | 0.7619 | 0.5327 | -0.1965 | -0.4465 | DA | DA |
| 40 | 0.4846 | 0.2720 | -0.3456 | 0.8566 | -0.5302 | -0.5475 | -0.5508 | -0.6135 | DOPA | DOPA |
| 41 | 0.1686 | 0.6606 | 2.0220 | -0.4324 | 0.4894 | 0.4269 | 0.2602 | 0.3227 | LNAA | LNAA |
| 42 | 1.3730 | 1.0540 | 1.4610 | 1.2590 | -0.5673 | -0.5465 | -0.6090 | -0.6715 | DOPAM | DOPAM |
| 43 | 0.1900 | 0.6440 | 2.0880 | -0.4437 | 0.4906 | 0.4281 | 0.2615 | 0.3240 | LNAA | LNAA |
| 44 | -0.2106 | 0.00066 | 0.8846 | 0.3986 | 0.6019 | 0.4521 | 0.3185 | 0.4073 | DA/LNAA 30%/70% | DA/LNAA 30%/70% |
| 45 | -0.4582 | -0.1373 | 0.4146 | 0.2966 | 0.5833 | 0.4823 | 0.3185 | 0.3479 | DA/LNAA 50%/50% | DA/LNAA 50%/50% |
| 46 | -0.1766 | -0.2506 | -0.02733 | -0.1086 | -0.4871 | -0.5319 | -0.5475 | -0.5767 | DA/DOPAM 50%/50% | DA/DOPAM 50%/50% |
| 47 | 0.1120 | 0.01333 | 0.1906 | 0.2773 | -0.5475 | -0.5319 | -0.5475 | -0.6371 | DA/DOPAM 30%/70% | DA/DOPAM 30%/70% |
| 48 | 0.1060 | 0.0600 | 0.1653 | 0.2606 | -0.5621 | -0.5621 | -0.5621 | -0.6254 | DA/DOPAM 30%/70% | DA/DOPAM 30%/70% |
| 49 | 0.4613 | 0.4080 | 0.5793 | 0.6680 | -0.5475 | -0.5769 | -0.5767 | -0.6808 | DA/DOPAM 10%/90% | DA/DOPAM 10%/90% |
| 50 | -0.5607 | -0.4600 | -0.0440 | -0.1913 | 0.5125 | 0.3927 | 0.2654 | 0.3071 | DA/LNAA 70%/30% | DA/LNAA 70%/30% |
| 51 | -0.08666 | 0.1220 | 1.3740 | 0.6726 | 0.5865 | 0.3779 | 0.3185 | 0.4227 | DA/LNAA 10%/90% | DA/LNAA 10%/90% |
| 52 | -0.0360 | 0.3973 | 1.3890 | 0.6886 | 0.5571 | 0.3925 | 0.2738 | 0.3925 | DA/LNAA 10%/90% | DA/LNAA 10%/90% |
| 53 | -0.2880 | 0.05733 | 0.7940 | 0.2960 | 0.5865 | 0.3185 | 0.3188 | 0.3779 | DA/LNAA 30%/70% | DA/LNAA 30%/70% |
| 54 | -0.1773 | -0.2320 | -0.0366 | -0.044 | -0.5173 | -0.5327 | -0.5923 | -0.5908 | DA/DOPAM 50%/50% | DA/DOPAM 50%/50% |
| 55 | -0.3572 | -0.1713 | 0.4033 | 0.1573 | 0.5717 | 0.4373 | 0.3217 | 0.3331 | DA/LNAA 50%/50% | DA/LNAA 50%/50% |
| 56 | 0.1006 | 0.0420 | 0.0687 | 0.2600 | -0.5444 | -0.5769 | -0.5510 | -0.6308 | DA/DOPAM 30%/70% | DA/DOPAM 30%/70% |
| 57 | -0.7391 | -0.6897 | -0.4780 | -0.5822 | -0.5319 | -0.5621 | -0.6006 | -0.6665 | DA/LNAA 90%/10% | DA/LNAA 90%/10% |
| 58 | -0.7343 | -0.6842 | -0.4676 | -0.5020 | -0.5621 | -0.6071 | -0.6069 | -0.6546 | DA/LNAA 90%/10% | DA/LNAA 90%/10% |
| 59 | -0.1880 | -0.2140 | -0.0326 | -0.0913 | -0.5027 | -0.5621 | -0.5769 | -0.6215 | DA/DOPAM 50%/50% | DA/DOPAM 50%/50% |
| 60 | -0.5481 | -0.4223 | -0.056 | -0.2906 | 0.5271 | 0.4073 | 0.2579 | 0.2996 | DA/LNAA 70%/30% | DA/LNAA 70%/30% |
| 61 | -0.0200 | 0.2913 | 1.3480 | 0.7866 | 0.4227 | 0.3956 | 0.3031 | 0.3958 | DA/LNAA 10%/90% | DA/LNAA 10%/90% |
| 62 | -0.2686 | -0.0173 | 0.8406 | 0.4546 | 0.4373 | 0.4375 | 0.3198 | 0.3917 | DA/LNAA 30%/70% | DA/LNAA 30%/70% |
| 63 | 0.5500 | 0.4533 | 0.7153 | 0.6886 | -0.5244 | -0.6158 | -0.6138 | -0.6575 | DA/DOPAM 10%/90% | DA/DOPAM 10%/90% |
| 64 | -0.7320 | -0.6905 | -0.4785 | -0.5532 | 0.4969 | 0.4348 | 0.2440 | 0.2581 | DA/LNAA 90%/10% | DA/LNAA 90%/10% |
| 65 | -0.4380 | -0.1580 | 0.3713 | 0.1773 | 0.4373 | 0.4073 | 0.3229 | 0.2883 | DA/LNAA 50%/50% | DA/LNAA 50%/50% |
| 66 | -0.5566 | -0.4216 | -0.016 | -0.2306 | 0.5865 | 0.3927 | 0.2608 | 0.3331 | DA/LNAA 70%/30% | DA/LNAA 70%/30% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 67 | 0.2687 | 0.202 | -0.3432 | 0.9267 | -0.4729 | -0.5166 | -0.5771 | -0.625 | DA/DOPA 50%/50% | DA/DOPA 50%/50% |
| 68 | 0.2313 | 0.086 | -0.34473 | 0.7287 | -0.4583 | -0.5208 | -0.5833 | -0.6042 | DA/DOPA 50%/50% | DA/DOPA 50%/50% |
| 69 | -0.3627 | -0.5647 | -0.56584 | -0.3892 | -0.5625 | -0.5667 | -0.55 | -0.5833 | DA/DOPA 70%/30% | DA/DOPA 70%/30% |
| 70 | -0.3802 | -0.5497 | -0.59792 | -0.4322 | -0.5583 | -1.0417 | -0.5520 | -0.575 | DA/DOPA 70%/30% | DA/DOPA 70%/30% |
| 71 | -0.1647 | -0.152 | 0.196 | 0.534 | -0.417 | 0.05 | 0.1167 | -0.3083 | DOPA/LNAA 50%/50% | DOPA/LNAA 50%/50% |
| 72 | -0.162 | -0.1507 | 0.1693 | 0.048 | -0.4125 | 0.05 | 0.1208 | -0.3125 | DOPA/LNAA 50%/50% | DOPA/LNAA 50%/50% |
| 73 | 0.2153 | -0.0633 | 0.1934 | 0.382 | -0.5 | -0.4875 | -0.40 | -0.5375 | DOPA/LNAA 70%/30% | DOPA/LNAA 70%/30% |
| 74 | 0.202 | 0.006 | 0.1193 | 0.3693 | -0.4958 | -0.4833 | -0.3958 | -0.5375 | DOPA/LNAA 70%/30% | DOPA/LNAA 70%/30% |
| 75 | 0.3367 | -0.0447 | 0.4407 | 0.504 | -0.5667 | -0.525 | -0.6458 | -0.6458 | DOPA/DOPAM 50%/50% | DOPA/DOPAM 50%/50% |
| 76 | 0.328 | -0.0747 | -0.0873 | 0.130 | -0.5625 | -0.5208 | -0.625 | -0.625 | DOPA/DOPAM 50%/50% | DOPA/DOPAM 50%/50% |
| 77 | -0.0407 | 0.08 | 0.6373 | 0.406 | -0.4208 | 0.1541 | 0.1708 | 0 | DOPAM/LNAA 50%/50% | DOPAM/LNAA 50%/50% |
| 78 | -0.0633 | 0.062 | 0.628 | 0.4453 | -0.3958 | 0.175 | 0.1667 | 0.02083 | DOPAM/LNAA 50%/50% | DOPAM/LNAA 50%/50% |
| 79 | -0.1173 | -0.0633 | 0.2813 | 0.1067 | -0.5875 | 0 | 0.0625 | -0.225 | DA/DOPA/LNAA 60%/20%/20% | DA/DOPA/LNAA 60%/20%/20% |
| 80 | -0.1207 | -0.1013 | 0.2893 | 0.2073 | -0.5833 | 0.0208 | 0.0729 | -0.2167 | DA/DOPA/LNAA 60%/20%/20% | DA/DOPA/LNAA 60%/20%/20% |
| 81 | -0.2107 | 0.322 | 1.301 | 0.8973 | 0.3333 | 0.3541 | 0.4167 | 0.4375 | LNAA/DA/DOPAM 60%/20%/20% | LNAA/DA/DOPAM 60%/20%/20% |
| 82 | -0.1853 | 0.4807 | 1.158 | 0.804 | 0.3541 | 0.375 | 0.4083 | 0.4583 | LNAA/DA/DOPAM 60%/20%/20% | LNAA/DA/DOPAM 60%/20%/20% |
| 83 | 0.9253 | 1.091 | 1.527 | 1.6367 | -0.5583 | -0.525 | -0.5667 | -0.1208 | DOPAM/LNAA/DOPA 60%/20%/20% | DOPAM/LNAA/DOPA 60%/20%/20% |
| 84 | 1.1307 | 1.033 | 1.6307 | 1.606 | -0.5417 | -0.5208 | -0.5625 | -0.125 | DOPAM/LNAA/DOPA 60%/20%/20% | DOPAM/LNAA/DOPA 60%/20%/20% |
| 85 | 1.531 | 1.604 | 2.2433 | 2.3327 | -0.5708 | -0.5833 | -0.6458 | -0.7167 | DOPA/LNAA/DA 60%/20%/20% | DOPA/LNAA/DA 60%/20%/20% |
| 86 | 1.564 | 1.579 | 1.972 | 2.2993 | -0.5625 | -0.6041 | -0.625 | -0.7083 | DOPA/LNAA/DA 60%/20%/20% | DOPA/LNAA/DA 60%/20%/20% |
| 87 | -0.2573 | -0.3127 | -0.126 | -0.2473 | -0.4458 | -0.2917 | -0.1958 | -0.0125 | DA/DOPA/LNAA/DOPAM 25%/25%/25%/25% | DA/DOPA/LNAA/DOPAM 25%/25%/25%/25% |
| 88 | -0.2913 | -0.3814 | 0.3733 | -0.103 | -0.4375 | -0.2708 | -0.1875 | 0 | DA/DOPA/LNAA/DOPAM 25%/25%/25%/25% | DA/DOPA/LNAA/DOPAM 25%/25%/25%/25% |