## SUPPORTING INFORMATION

## Mixed-ligand Pt(II) dithione-dithiolato complexes: influence of the dicyanobenzodithiolato ligand on the second-order-NLO Properties

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List of bond distances [Å] and angles [deg] for  $[Pt(Bz_2pipdt)(dcbdt)]$  (Table S1) and DFT optimized geometries for  $[Pt(Bz_2pipdt)(dcbdt)]$  and  $[Pt(Bz_2pipdt)(dmit)]$  (Tables S2 and S3); drawing, relative energy and percent compositions of the most significant orbitals obtained by DFT calculations in vacuum and in DMF for  $[Pt(Bz_2pipdt)(dcbdt)]$  and  $[Pt(Bz_2pipdt)(dmit)]$  (Tables S4 and S5); Simulated visible spectra for  $[Pt(Bz_2pipdt)(dcbdt)]$  and  $[Pt(Bz_2pipdt)(dmit)]$  (Figures S1 and S2).

| $\begin{array}{c} \text{Pt}-\text{S}(2)\\ \text{Pt}-\text{S}(2) \#1\\ \text{Pt}-\text{S}(1)\\ \text{Ft}-\text{S}(1)\\ \text{S}(2)-\text{C}(10)\\ \text{S}(1)-\text{C}(1)\\ \text{C}(10)-\text{C}(10) \#1\\ \text{C}(10)-\text{C}(11)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(1)-\text{C}(1)\\ \text{C}(12)-\text{C}(12)\\ \text{H}1\\ \text{C}(12)-\text{C}(12)\\ \text{H}1\\ \text{C}(12)-\text{C}(13)\\ \text{N}(1)-\text{C}(2)\\ \text{N}(1)-\text{C}(2)\\ \text{N}(1)-\text{C}(3)\\ \text{C}(2)-\text{C}(2) \#1\\ \text{C}(2)-\text{H}(2A)\\ \text{C}(2)-\text{H}(2B)\\ \text{C}(11)-\text{H}(11)\\ \text{C}(13)-\text{N}(2)\\ \text{C}(5)-\text{C}(6)\\ \text{C}(5)-\text{H}(5)\\ \text{C}(3)-\text{H}(3A)\\ \text{C}(3)-\text{H}(3B)\\ \text{C}(6)-\text{C}(7)\\ \text{C}(6)-\text{H}(6)\\ \text{C}(9)-\text{C}(8)\\ \text{C}(9)-\text{H}(9)\\ \text{C}(7)-\text{C}(8)\\ \text{C}(7)-\text{H}(7)\\ \text{C}(8)-\text{H}(8)\\ \end{array}$ | 2.2734(10)<br>2.2734(10)<br>2.2784(10)<br>2.2784(10)<br>1.751(4)<br>1.688(4)<br>1.390(7)<br>1.392(5)<br>1.371(6)<br>1.386(7)<br>1.515(6)<br>1.323(4)<br>1.484(8)<br>1.380(6)<br>1.411(9)<br>1.443(6)<br>1.467(5)<br>1.470(5)<br>1.424(9)<br>0.9700<br>0.9700<br>0.9700<br>0.9700<br>1.125(6)<br>1.395(8)<br>0.9300<br>1.366(9)<br>0.9300<br>1.338(9)<br>0.9300<br>0.9300 |
|--|--|
| S(2) - Pt - S(2) #1<br>S(2) - Pt - S(1) #1<br>S(2) #1 - Pt - S(1) #1<br>S(2) #1 - Pt - S(1)<br>S(1) #1 - Pt - S(1)<br>C(10) - S(2) - Pt<br>C(1) - S(1) - Pt<br>C(10) #1 - C(10) - C(11)<br>C(10) #1 - C(10) - S(2)<br>C(11) - C(10) - S(2)<br>C(9) - C(4) - C(5)<br>C(9) - C(4) - C(3)<br>C(5) - C(4) - C(3)<br>N(1) - C(1) - C(1) #1<br>N(1) - C(1) - S(1)<br>C(1) #1 - C(1) - S(1)<br>C(11) - C(12) - C(12) #1<br>C(11) - C(12) - C(13)<br>C(1) - N(1) - C(2)  | 89.88(5)<br>177.25(4)<br>90.99(4)<br>90.99(4)<br>177.25(4)<br>88.27(5)<br>103.73(13)<br>105.76(14)<br>119.7(2)<br>121.33(12)<br>118.9(3)<br>119.1(5)<br>120.8(4)<br>120.0(4)<br>119.6(2)<br>120.6(3)<br>119.87(14)<br>119.5(3)<br>120.4(4)<br>120.1(2)<br>120.5(3)   |

Table S1. Bond lengths [Å] and angles [deg] for [Pt(Bz<sub>2</sub>pipdt)(dcbdt)].

| C(1) - N(1) - C(3)<br>C(2) - N(1) - C(3)   | 121.9(3)<br>117.2(3) |
|--|----------------------|
| C(2) #1 - C(2) - N(1)                      | 115.1(3)             |
| U(2) + I - U(2) - H(2A)                    | 108.5                |
| $C(2) \pm 1 - C(2) - H(2B)$                | 108.5                |
| N(1) - C(2) - H(2B)                        | 108.5                |
| H(2A) - C(2) - H(2B)                       | 107.5                |
| C(12) - C(11) - C(10)                      | 120.7(4)             |
| C(12) - C(11) - H(11)                      | 119.7                |
| C(10)-C(11)-H(11)                          | 119.7                |
| N(2) - C(13) - C(12)                       | 178.9(6)             |
| C(4)-C(5)-C(6)                             | 119.9(6)             |
| C(4) - C(5) - H(5)                         | 120.1                |
| C(6) - C(5) - H(5)                         | 120.1                |
| N(1) - C(3) - C(4)                         | 113.8(3)             |
| N(1) - C(3) - H(3A)                        | 108.8                |
| C(4) - C(3) - H(3A)<br>N(1) $C(2)$ $H(3B)$ | 108.8                |
| N(1) - C(3) - H(3B)<br>C(4) - C(2) - H(3B) | 100.0                |
| $U(2\lambda) = C(2) = U(2D)$               | 100.0                |
| C(7) - C(6) - C(5)                         | 107.7<br>118 9(7)    |
| C(7) - C(6) - H(6)                         | 120 6                |
| C(5) - C(6) - H(6)                         | 120.6                |
| C(8) - C(9) - C(4)                         | 120.0(6)             |
| C(8) - C(9) - H(9)                         | 120.0                |
| C(4) - C(9) - H(9)                         | 120.0                |
| C(8) - C(7) - C(6)                         | 120.9(7)             |
| C(8)-C(7)-H(7)                             | 119.5                |
| C(6) - C(7) - H(7)                         | 119.5                |
| C(7)-C(8)-C(9)                             | 121.2(7)             |
| С(7)-С(8)-Н(8)                             | 119.4                |
| C(9) - C(8) - H(8)                         | 119.4                |

atoms:

Symmetry transformations used to generate equivalent

#1 -x+1,y,-z+1/2

| JIIC | J(u,p)-5DD | ).       |          |
|------|------------|----------|----------|
| С    | 3.34176    | 6.07453  | 1.16719  |
| С    | 3.90209    | 4.91259  | 1.69180  |
| С    | 2.87109    | 6.08104  | -0.14407 |
| С    | 3.99769    | 3.76562  | 0.90721  |
| С    | 2.96139    | 4.93185  | -0.92439 |
| С    | -7.50807   | 1.36655  | -0.49032 |
| С    | 3.52927    | 3.76534  | -0.40740 |
| С    | -6.28788   | 0.66917  | -0.24011 |
| С    | -5.07616   | 1.31168  | -0.47031 |
| С    | -7.50805   | -1.36664 | 0.49035  |
| С    | -6.28788   | -0.66925 | 0.24013  |
| С    | -3.85448   | 0.66407  | -0.23828 |
| С    | -5.07614   | -1.31175 | 0.47031  |
| С    | -3.85447   | -0.66413 | 0.23827  |
| С    | 4.86461    | -0.46050 | 0.60104  |
| С    | 3.67751    | -2.55108 | 1.31234  |
| С    | 2.45559    | 0.66859  | -0.29270 |
| С    | 3.67747    | 2.55116  | -1.31232 |
| С    | 2.45560    | -0.66854 | 0.29270  |
| С    | 4.86460    | 0.46057  | -0.60105 |
| С    | 3.52937    | -3.76528 | 0.40742  |
| С    | 2.96154    | -4.93181 | 0.92442  |
| С    | 3.99778    | -3.76554 | -0.90719 |
| С    | 2.87129    | -6.08101 | 0.14410  |
| С    | 3.90223    | -4.91253 | -1.69177 |
| С    | 3.34196    | -6.07448 | -1.16715 |
| Н    | 3.26323    | 6.96580  | 1.77869  |
| Н    | 4.26156    | 4.89653  | 2.71440  |
| Н    | 2.42104    | 6.97683  | -0.55615 |
| Н    | 4.42428    | 2.86315  | 1.33073  |
| Н    | 2.57586    | 4.93910  | -1.93884 |
| Н    | -5.07946   | 2.33139  | -0.83517 |
| Н    | 4.95825    | 0.12080  | 1.52818  |
| Н    | 2.89564    | -2.56757 | 2.07758  |
| Н    | 4.63738    | -2.59693 | 1.83426  |
| Н    | -5.07943   | -2.33146 | 0.83518  |
| Н    | 5.71671    | 1.13858  | -0.53914 |
| Н    | 5.71673    | -1.13849 | 0.53912  |
| Н    | 4.63735    | 2.59703  | -1.83422 |
| Н    | 2.89561    | 2.56763  | -2.07758 |
| Н    | 2.57602    | -4.93907 | 1.93887  |
| Н    | 4.95824    | -0.12072 | -1.52819 |
| Н    | 4.42432    | -2.86306 | -1.33071 |
| Н    | 2.42128    | -6.97682 | 0.55619  |
| Н    | 4.26170    | -4.89646 | -2.71437 |
| Н    | 3.26346    | -6.96577 | -1.77864 |
| N    | -8.48118   | 1.95285  | -0.70131 |
| Ν    | -8.48115   | -1.95296 | 0.70135  |
| Ν    | 3.63977    | -1.25764 | 0.62217  |
| N    | 3.63975    | 1.25770  | -0.62217 |
| S    | -2.35902   | 1.52678  | -0.54495 |
| S    | 0.99511    | 1.49705  | -0.57250 |
| S    | -2.35900   | -1.52682 | 0.54492  |
| S    | 0.99514    | -1.49704 | 0.57247  |
| Pt   | -0.70800   | -0.00001 | -0.00001 |
|      |            |          |          |

**Table S2**. Cartesian coordinates of the optimized complex [Pt(Bz2pipdt)(dcbdt)] (B3LYP/6-311G(d,p)-SDD).



B3LYP/6-311G(d,p)-SDD



X-Ray

**Table S3**. Cartesian coordinates of the optimized complex [Pt(Bz2pipdt)(dmit)] (B3LYP/6-311G(d,p)-SDD).

| Pt         3.737352         3.974797         2.039873           S         3.897323         -0.69005         7.671681           S         4.435691         6.155474         1.629329           S         4.576006         4.031299         4.213163           S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.60235         9.277251 | 5110 | J(u,p)-SDD) | •                 |                   |
|---|------|-------------|-------------------|-------------------|
| S         3.897323         -0.69005         7.671681           S         4.435691         6.155474         1.629329           S         4.576006         4.031299         4.213163           S         2.971132         1.806579         2.416007           S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.35426         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.60235         9.277251   | Pt   | 3.737352    | 3.974797          | 2.039873          |
| S         4.435691         6.155474         1.629329           S         4.576006         4.031299         4.213163           S         2.971132         1.806579         2.416007           S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.34226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.847512         8.844009         0.24637           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         2.759183         9.64115   | S    | 3.897323    | -0.69005          | 7.671681          |
| S         4.576006         4.031299         4.213163           S         2.971132         1.806579         2.416007           S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         2.759183         9.64115         1.489597           H         2.594209         8.626068  | S    | 4.435691    | 6.155474          | 1.629329          |
| S         2.971132         1.806579         2.416007           S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.60235         9.277251         -0.39461           H         5.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976    | S    | 4.576006    | 4.031299          | 4.213163          |
| S         2.965067         3.951645         -0.15434           S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115     | S    | 2.971132    | 1.806579          | 2.416007          |
| S         3.118522         -0.00447         4.849784           S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068     | S    | 2.965067    | 3.951645          | -0.15434          |
| S         4.561225         1.974996         6.448397           N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         3.361317         0.35955      | S    | 3.118522    | -0.00447          | 4.849784          |
| N         4.201067         7.74828         -0.50645           C         3.981668         6.504392         0.011454           C         3.364226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         5.395486         2.9389      | S    | 4.561225    | 1.974996          | 6.448397          |
| C         3.981668         6.504392         0.011454           C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.85559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.3651317         0.35955     | Ν    | 4.201067    | 7.74828           | -0.50645          |
| C         3.46912         1.531152         4.056056           C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.363622         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791       | С    | 3.981668    | 6.504392          | 0.011454          |
| C         3.354226         5.488123         -0.8125           N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.668399           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791       | С    | 3.46912     | 1.531152          | 4.056056          |
| N         3.08275         5.758624         -2.12275           C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         2.093795         11.96398         1.457683           H         4.264875         2.37791         -4.28542           C         2.093795         11.96398     | С    | 3.354226    | 5.488123          | -0.8125           |
| C         2.451339         4.79758         -3.03791           H         1.643637         5.324837         -3.55613           H         1.9919         4.012509         -2.43888           C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         2.093795         11.96398         1.457683           H         4.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884    | N    | 3.08275     | 5.758624          | -2.12275          |
| H1.6436375.324837-3.55613H1.99194.012509-2.43888C4.8275128.8440090.24637H5.602359.277251-0.39461H5.3284698.4151051.113174C3.4059254.207046-4.0609C4.1414052.4581914.80483C3.8555599.9319760.66839C2.7591839.641151.489597H2.5942098.6260681.832767C4.5368223.484996-3.65998H4.7415823.341786-2.60503C3.8613170.359556.40452C5.3954862.9389-4.60878H6.2648752.37791-4.28542C2.09379511.963981.457683H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.08927.175931-3.64289H3.0536613.280540.313471C3.657566.951444-2.73853H3.0892 <td< td=""><td>С</td><td>2.451339</td><td>4.79758</td><td>-3.03791</td></td<>   | С    | 2.451339    | 4.79758           | -3.03791          |
| H1.99194.012509-2.43888C4.8275128.8440090.24637H5.602359.277251-0.39461H5.3284698.4151051.113174C3.4059254.207046-4.0609C4.1414052.4581914.80483C3.8555599.9319760.66839C2.7591839.641151.489597H2.5942098.6260681.832767C4.5368223.484996-3.65998H4.7415823.341786-2.60503C3.8613170.359556.40452C5.3954862.9389-4.60878H6.2648752.37791-4.28542C2.09379511.963981.457683H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.573069 <td< td=""><td>Н</td><td>1.643637</td><td>5.324837</td><td>-3.55613</td></td<>   | Н    | 1.643637    | 5.324837          | -3.55613          |
| C         4.827512         8.844009         0.24637           H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066      | Н    | 1.9919      | 4.012509          | -2.43888          |
| H         5.60235         9.277251         -0.39461           H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         2.80176         4.922013      | С    | 4.827512    | 8.844009          | 0.24637           |
| H         5.328469         8.415105         1.113174           C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579     | Н    | 5.60235     | 9.277251          | -0.39461          |
| C         3.405925         4.207046         -4.0609           C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.668399           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332      | Н    | 5.328469    | 8.415105          | 1.113174          |
| C         4.141405         2.458191         4.80483           C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579       | С    | 3.405925    | 4.207046          | -4.0609           |
| C         3.855559         9.931976         0.66839           C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         3.042165         10.41332       | С    | 4.141405    | 2.458191          | 4.80483           |
| C         2.759183         9.64115         1.489597           H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         2.04203         3.815237         -6.3767           H         3.801868         3.945076        | С    | 3.855559    | 9.931976          | 0.66839           |
| H         2.594209         8.626068         1.832767           C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076     | С    | 2.759183    | 9.64115           | 1.489597          |
| C         4.536822         3.484996         -3.65998           H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228      | Н    | 2.594209    | 8.626068          | 1.832767          |
| H         4.741582         3.341786         -2.60503           C         3.861317         0.35955         6.40452           C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.035366         13.28054      | С    | 4.536822    | 3.484996          | -3.65998          |
| C3.8613170.359556.40452C5.3954862.9389-4.60878H6.2648752.37791-4.28542C2.09379511.963981.457683H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | Н    | 4.741582    | 3.341786          | -2.60503          |
| C         5.395486         2.9389         -4.60878           H         6.264875         2.37791         -4.28542           C         2.093795         11.96398         1.457683           H         1.412616         12.74884         1.765763           C         4.055285         11.2491         0.24958           H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.353366         13.28054         0.313471           C         3.65756         6.951444         -2.73853           H         3.0892         7.175931       | С    | 3.861317    | 0.35955           | 6.40452           |
| H6.2648752.37791-4.28542C2.09379511.963981.457683H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | С    | 5.395486    | 2.9389            | -4.60878          |
| C2.09379511.963981.457683H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | Н    | 6.264875    | 2.37791           | -4.28542          |
| H1.41261612.748841.765763C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.05336613.280540.313471C3.657566.951444-2.73853H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | С    | 2.093795    | 11.96398          | 1.457683          |
| C4.05528511.24910.24958H4.9035111.48807-0.38451C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | Н    | 1.412616    | 12.74884          | 1.765763          |
| H         4.90351         11.48807         -0.38451           C         3.15547         4.367251         -5.42535           H         2.280176         4.922013         -5.749           C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.353366         13.28054         0.313471           C         3.65756         6.951444         -2.73853           H         3.0892         7.175931         -3.64289           H         4.69737         6.768077         -3.03422           C         3.573069         8.114411         -1.77293           H         4.104393         8.976384         -2.18037           H         2.529436         8.410194         -1.61292   | С    | 4.055285    | 11.2491           | 0.24958           |
| C3.155474.367251-5.42535H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | Н    | 4.90351     | 11.48807          | -0.38451          |
| H2.2801764.922013-5.749C1.88434510.650661.878553H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | С    | 3.15547     | 4.367251          | -5.42535          |
| C         1.884345         10.65066         1.878553           H         1.042165         10.41332         2.51848           C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.353366         13.28054         0.313471           C         3.65756         6.951444         -2.73853           H         3.0892         7.175931         -3.64289           H         4.69737         6.768077         -3.03422           C         3.573069         8.114411         -1.77293           H         4.104393         8.976384         -2.18037           H         2.529436         8.410194         -1.61292  | Н    | 2.280176    | 4.922013          | -5.749            |
| H1.04216510.413322.51848C5.1353553.101579-5.96953H5.8041432.671453-6.70618C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | С    | 1.884345    | 10.65066          | 1.878553          |
| C         5.135355         3.101579         -5.96953           H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.353366         13.28054         0.313471           C         3.65756         6.951444         -2.73853           H         3.0892         7.175931         -3.64289           H         4.69737         6.768077         -3.03422           C         3.573069         8.114411         -1.77293           H         4.104393         8.976384         -2.18037           H         2.529436         8.410194         -1.61292   | Н    | 1.042165    | 10.41332          | 2.51848           |
| H         5.804143         2.671453         -6.70618           C         4.012303         3.815237         -6.3767           H         3.801868         3.945076         -7.4322           C         3.182352         12.26228         0.643813           H         3.353366         13.28054         0.313471           C         3.65756         6.951444         -2.73853           H         3.0892         7.175931         -3.64289           H         4.69737         6.768077         -3.03422           C         3.573069         8.114411         -1.77293           H         4.104393         8.976384         -2.18037           H         2.529436         8.410194         -1.61292  | С    | 5.135355    | 3.101579          | -5.96953          |
| C4.0123033.815237-6.3767H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | Н    | 5.804143    | 2.671453          | -6.70618          |
| H3.8018683.945076-7.4322C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | С    | 4.012303    | 3.815237          | -6.3767           |
| C3.18235212.262280.643813H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | Н    | 3.801868    | 3.945076          | -7.4322           |
| H3.35336613.280540.313471C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | С    | 3.182352    | 12.26228          | 0.643813          |
| C3.657566.951444-2.73853H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | Н    | 3.353366    | 13.28054          | 0.313471          |
| H3.08927.175931-3.64289H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | С    | 3.65756     | 6.951444          | -2.73853          |
| H4.697376.768077-3.03422C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | Н    | 3.0892      | 7.175931          | -3.64289          |
| C3.5730698.114411-1.77293H4.1043938.976384-2.18037H2.5294368.410194-1.61292   | Н    | 4.69737     | 6.768077          | -3.03422          |
| H4.1043938.976384-2.18037H2.5294368.410194-1.61292  | С    | 3.573069    | 8.114411          | -1.77293          |
| H 2.529436 8.410194 -1.61292  | Н    | 4.104393    | 8.976384          | -2.18037          |
|   | Н    | 2.529436    | 8. <u>4</u> 10194 | -1. <u>61</u> 292 |



B3LYP/6-311G(d,p)-SDD

X-Ray

|        |                  | E (eV ) | Fragment composition (%) |                       |       |  |  |
|--------|------------------|---------|--------------------------|-----------------------|-------|--|--|
|        |                  |         | Pt                       | Bz <sub>2</sub> pipdt | debdt |  |  |
| LUMO+3 |                  | -1.12   | 1.4                      | 98.4                  | 0.1   |  |  |
| LUMO+2 | ****             | -1.47   | 1.1                      | 0.0                   | 98.9  |  |  |
| LUMO+1 | Care Contraction | -1.88   | 33.7                     | 30.0                  | 36.3  |  |  |
| LUMO   |                  | -3.85   | 6.3                      | 78.4                  | 15.3  |  |  |
| номо   | \$ <b>~\$¢</b> < | -5.47   | 8.4                      | 23.3                  | 68.3  |  |  |
| HOMO-1 | ****             | -5.91   | 18.8                     | 4.5                   | 76.7  |  |  |
| НОМО-2 |                  | -7.01   | 81.3                     | 4.5                   | 14.2  |  |  |
| НОМО-3 |                  | -7.10   | 20.6                     | 54.3                  | 25.2  |  |  |
| НОМО-4 | \$000C           | -7.16   | 28.5                     | 29.2                  | 42.3  |  |  |

**Table S4**. MOs diagrams of [Pt(Bz2pipdt)(dcbdt)] in the gas-phase (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals

**Table S5**. MOs diagrams of [Pt(Bz2pipdt)(dcbdt)] in the solution phase, DMF, (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals.

|        |  | E (eV ) | Fragment composition (%) |                       |       |  |  |
|--------|--|---------|--------------------------|-----------------------|-------|--|--|
| 2      |  |         | Pt                       | Bz <sub>2</sub> pipdt | dcbdt |  |  |
| LUMO+3 | ¢~~•;<   | -1.35   | 0.3                      | 0.0                   | 99.7  |  |  |
| LUMO+2 | Contraction of the second seco | -1.85   | 34.5                     | 30.1                  | 35.4  |  |  |
| LUMO+1 |  | -1.99   | 1.1                      | 0.0                   | 98.9  |  |  |
| LUMO   |  | -3.72   | 4.6                      | 88.2                  | 7.2   |  |  |
| номо   | <b>\$~\$¢</b> <  | -5.64   | 13.7                     | 17.6                  | 68.7  |  |  |
| HOMO-1 |  | -6.10   | 26.8                     | 10.7                  | 62.5  |  |  |
| НОМО-2 |  | -6.87   | 85.0                     | 6.2                   | 8.8   |  |  |
| НОМО-3 |  | -6.99   | 3.0                      | 87.2                  | 9.8   |  |  |
| НОМО-4 |  | -7.05   | 0.8                      | 96.5                  | 2.7   |  |  |

|        |  | E (eV ) | Fragment composition (%) |                       |       |  |  |
|--------|--|---------|--------------------------|-----------------------|-------|--|--|
|        | 14.0                                   |         | Pt                       | Bz <sub>2</sub> pipdt | debdt |  |  |
| LUMO+3 |  | -1.16   | 0.7                      | 00.0                  | 0.3   |  |  |
| LUMO+2 | ************************************** | -1.61   | 0.0                      | 0.0                   | 100   |  |  |
| LUMO+1 |  | -1.94   | 33.3                     | 30.9                  | 35.8  |  |  |
| LUMO   |  | -3.70   | 5.5                      | 70.6                  | 23.9  |  |  |
| НОМО   | ₩<br>₩<br>₩                            | -4.96   | 3.1                      | 27.2                  | 69.7  |  |  |
| HOMO-1 |  | -6.00   | 0.6                      | 0.9                   | 98.6  |  |  |
| НОМО-2 |  | -6.12   | 28.7                     | 15.5                  | 55.8  |  |  |
| НОМО-3 |  | -6.24   | 15.1                     | 14.7                  | 70.2  |  |  |
| НОМО-4 |  | -6.93   | 74.9                     | 11.1                  | 14.0  |  |  |

**Table S6**. MOs diagrams of [Pt(Bz2pipdt)(dmit)] in the gas-phase (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals

| Table    | <b>S7</b> . | MOs   | diagram  | s of | [Pt( | (Bz2pipdt)(d | mit)] | in   | the  | solution  | phase, | DMF,    | (B3 | 3LYP/6- |
|----------|-------------|-------|----------|------|------|--------------|-------|------|------|-----------|--------|---------|-----|---------|
| 311G(d   | 1,p)-1      | SDD), | together | with | the  | contributio  | n of  | diff | eren | t fragmen | nts to | complex | es  | valence |
| orbitals | 5.          |       |          |      |      |              |       |      |      |           |        |         |     |         |

|        |  | E (eV ) | Fragment composition (%) |                       |      |  |  |
|--------|--|---------|--------------------------|-----------------------|------|--|--|
|        |  |         | Pt                       | Bz <sub>2</sub> pipdt | dmit |  |  |
| LUMO+3 |  | -0.87   | 2.8                      | 3.5                   | 93.7 |  |  |
| LUMO+2 | T SHOULD   | -2.05   | 33.9                     | 30.5                  | 35.6 |  |  |
| LUMO+1 |  | -2.15   | 0.0                      | 0.0                   | 100  |  |  |
| LUMO   |  | -3.74   | 4.4                      | 84.6                  | 11.0 |  |  |
| номо   |  | -5.26   | 6.0                      | 17.0                  | 77.0 |  |  |
| HOMO-1 | 1000 - 100 - | -6.29   | 33.8                     | 25.8                  | 40.4 |  |  |
| НОМО-2 |  | -6.57   | 20.7                     | 23.6                  | 55.7 |  |  |
| НОМО-3 | **************************************   | -6.64   | 0.6                      | 1.6                   | 97.8 |  |  |
| HOMO-4 |  | -6.92   | 85.8                     | 6.1                   | 8.1  |  |  |



**Figure S1**. Simulated UV-vis spectrum of [Pt(Bz<sub>2</sub>pipdt)(dcbdt)]. Calculation were performed with the CPCM method (DMF, blue; CHCl3, red) and in Void (green), B3LYP/6-311G(d,p)-SDD.



**Figure S2**. Simulated UV-vis spectrum of [Pt(Bz<sub>2</sub>pipdt)(dmit)]. Calculation were performed with the CPCM method (DMF, blue; CHCl3, red) and in Void (green), B3LYP/6-311G(d,p)-SDD.