Supporting Information for
Active Learning Exploration of Transition Metal Complexes to Discover Method-Insensitive and Synthetically Accessible Chromophores
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Text S1. List of abbreviations used in the main text.
ML: machine learning
VHTS: virtual high throughput screening
DFT: density functional theory
DFA: density functional approximation
TMC: transition metal complex
CSD: Cambridge Structural Database
TDDFT: time-dependent DFT
MLCT: metal-ligand charge transfer
LS: low spin
HS: high spin
MR: multireference
Figure S1. Normalized histogram for the average ground state spin ($<\text{GS}>$) of the gen-0 complexes, with 0 corresponding to the case where all 23 DFAs agree on the assignment of LS as the ground state and 1 corresponding to the case where all 23 DFAs agree on the assignment of HS as the ground state.

Figure S2. $\Delta$-SCF gap computed at the HS versus the LS optimized geometry for the gen-0 complexes computed by B3LYP. The parity is shown as a black dashed line.
Figure S3. Δ-SCF gap computed at the LS optimized geometry for the gen-0 complexes computed by BLYP (x axis) and M06-2X (y axis). The parity is shown as a black dashed line.

Table S1. Ground state (GS) label with respect to the number and percentage of DFAs that determine LS to be the GS.

| label               | number (n) of DFAs | percentage (p) of DFAs |
|---------------------|--------------------|------------------------|
| consensus LS (0)    | n > 16             | p > 70%                |
| no consensus (1)    | 16 ≥ n > 6         | 70% ≥ p > 30%          |
| consensus HS (2)    | n ≤ 6              | p ≤ 30%                |

Figure S4. Normalized stacked histogram for $r_{ND}$ of optimized structures of the LS (red) and HS (blue) state for gen-0 complexes with box plots indicating their mean values and standard deviations at the top.
Figure S5. Model AUC for ground spin state classification from gen-0 to gen-6. At each generation, the ML models are trained on the combined training set of all previous generations and are tested on the set-aside test set of each generation separately. Since the number of complexes in each class and generation is small (after gen-0), the relative AUC of different models within each data generation is more meaningful than the comparisons of AUC from different data generations.

Figure S6. Percentage of TMCs retained versus the cutoff in 2D P[I] evaluated on the entire base TMC space. The location of a 2D P[I] = 1/3 (red, 0.02%) and 1/6 (green, 1.01%) is highlighted. Both x-axis and y-axis are in log scale.
Figure S7. Box plot for $r_{ND}$ computed only on the ligands of the 2,432 complexes with 2D PI $> 1/6$ evaluated by gen-3 ML models (green) and the 1.3M base complexes (blue). For each box, the median is shown as a horizontal solid line, the mean and std. dev. are shown as a dashed diamond, and the two extrema are shown by the vertical bar. Note that the $r_{ND}$ is computed on ligands instead of transition metal complexes. Due to the ligand additivity effect, the model favors low-$r_{ND}$ ligands although the model has only seen the whole complexes.

Table S2. Summary of $\Delta$-SCF gap and $r_{ND}$ for the other functionalized counterpart of complex F in the main text. The use of “--” corresponds to the case with no functionalization. Complex F is shaded in blue.

| depth ($d$) | functional group | $|\Delta$-SCF gap| (eV) | $r_{ND}$ |
|------------|------------------|-----------------|--------|--------|
| --         | --               | 2.82            | 0.301  |
| 3          | CH$_3$           | 2.38            | 0.306  |
| 4          | CH$_3$           | 3.04            | 0.288  |
| 4          | NH$_2$           | 3.17            | 0.309  |
| 5          | Cl               | 3.14            | 0.301  |
| 5          | F                | 2.81            | 0.302  |

Table S3. Summary of the properties for the first three excited states for the three complexes that lie on the Pareto front but do not have desired excited state properties.

| $|\Delta$-SCF gap| (eV) | $r_{ND}$ | 1$^{st}$ excited state | 2$^{nd}$ excited state | 3$^{rd}$ excited state |
|----------------|--------|--------|------------------------|------------------------|------------------------|
|                |        |        | energy (eV) | $f_{osc}$ (a.u.) | energy (eV) | $f_{osc}$ (a.u.) | energy (eV) | $f_{osc}$ (a.u.) |
| 3.40           | 0.256  | 2.50   | 0.001          | 2.57                  | 0.001          | 2.64                  | 0.000          |
| 2.48           | 0.299  | 2.43   | 0.001          | 2.48                  | 0.002          | 2.56                  | 0.002          |
| 3.01           | 0.269  | 2.28   | 0.000          | 2.50                  | 0.000          | 2.51                  | 0.000          |
Table S4. Summary of 13 randomly chosen complexes in gen-0 that fulfill the $\Delta$-SCF gap requirement (i.e., $< 3.5$ eV) by certain DFAs but violate either the consensus LS ground state or consensus low $\Delta$-SCF gap requirement. The ligand ID is our internal database ID, for which the corresponding geometry can be found in the Supporting Information Data. The two complexes that have promising excited state properties (i.e. with both bright state transition energy $< 3.5$ eV and MLCT character) are shaded in blue.

| metal | Ligand ID and count | $\Delta$-SCF gap I (eV) | Lowest $\Delta$-SCF gap (eV) and the corresponding DFA | Consensus $\Delta$-SCF gap | Consensus LS ground state | Consensus LS ground state and its $f_{osc}$ (a.u.) | 1st bright state energy (eV) and its $f_{osc}$ (a.u.) | MLCT state |
|-------|---------------------|------------------------|------------------------------------------------------|---------------------------|--------------------------|-------------------------------------------------|-----------------------------------------------|-----------|
| Fe    | 5fad526535c34d07 3da2144a (1) 5fad590e35c34d07 3da202cc (2) | 2.51 | 1.61 (MN15) | Yes | No | 3.88 (0.043) | Yes |
| Co    | 5fad527a35c34d07 3da22278 (2) 5fad58135c34d07 3da30b47 (1) | 3.69 | 2.99 (M06-2X) | No | Yes | 3.52 (0.518) | No |
| Co    | 5fad579235c34d07 3da2aeb7 (1) 5fad678135c34d07 3da3510d (2) | 3.92 | 3.42 (M06) | No | Yes | 3.58 (0.458) | Yes |
| Fe    | 5fad567435c34d07 3da2994c (2) 5fad561035c34d07 3da2da94 (1) | 4.29 | 3.38 (MN15) | No | Yes | 2.71 (0.153) | Yes |
| Co    | 5fad525f35c34d07 3da20be8 (1) 5fad542a35c34d07 3da28ae3 (2) | 3.83 | 3.44 (SCAN0) | No | Yes | 4.07 (0.044) | Yes |
| Co    | 5fad55d135c34d07 3da28e00 (1) 5fad52a935c34d07 3da2336 (2) | 3.82 | 3.43 (MN15-L) | No | Yes | 4.11 (0.780) | No |
| Fe    | 5fad526235c34d07 3da201de (2) 5fad52ca35c34d07 3da23b96 (1) | 5.06 | 3.23 (MN15) | No | No | 3.35 (0.092) | No |
| Fe    | 5fad526b35c34d07 3da219c0 (2) 5fad52ac35c34d07 3da2452 (1) | 4.68 | 3.46 (MN15) | No | No | 4.78 (0.578) | No |
| Fe    | 5fad54ac35c34d07 3da2770 (1) 5fad591135c34d07 3da20c0 (2) | 3.61 | 3.36 (PBE0) | No | No | 3.80 (0.043) | Yes |
| Fe    | 5fad527935c34d07 3da2226 (2) 5fad57da35c34d07 3da2af9c (1) | 4.79 | 3.46 (MN15) | No | No | 3.93 (0.272) | No |
| Fe    | 5fad62ee35c34d07 3da32b44 (2) 5fad55d135c34d07 3da28e00 (1) | 4.36 | 3.15 (MN15) | No | No | 3.75 (0.096) | Yes |
| Co    | 5fad528335c34d07 3da2266 (2) 5fad565d35c34d07 3da2976c (1) | 3.84 | 2.91 (SCAN0) | No | No | 3.22 (0.220) | Yes |
| Co    | 5fad5a7735c34d07 3da2d96 (2) 5fad5e5835c34d07 3da2f9a (1) | 3.23 | 2.94 (B3PW91) | Yes | No | 3.70 (0.150) | Yes |
Table S5. Summary of ligands in complexes A–F that have parent complexes in CSD that demonstrate interesting photo-induced properties and the associated references. The complex ID corresponds to the index of the six complexes in Figure 6 of the main text. The ligand ID is our internal database ID, for which the corresponding geometry can be found in the Supporting Information Data. For each ligand, the refcode for the CSD complex that contains this ligand and demonstrates interesting photo-induced properties is also shown.

| complex ID       | ligand ID       | ligand chemical name                                                                 | CSD refcode | relevant property and reference                  |
|------------------|-----------------|--------------------------------------------------------------------------------------|-------------|--------------------------------------------------|
| F                | 5fad527635c34d073da22057 | 4',5'-diaza-9'-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)fluorene                   | MIVSIU      | nonlinear optical property¹                        |
| E                | 5fad60c035c34d073da31750  | 2-(2,6-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline                        | ROVSEC      | peak of UV-vis spectra in the visible light region²|
| D                | 5fad528035c34d073da22500  | 1,2-bis(dimethylphosphino)ethane                                                    | JUWKOD      | luminescence³                                     |
| A, C, D          | 5fad542a35c34d073da26ae3  | Bis(1-methylimidazol-2-yl)-(4-methoxyphen-1-yl)methanol                              | EWEWAE      | peak of UV-vis spectra in the visible light region⁴|
| B                | 5fad67af35c34d073da3526f  | 1,2-bis(phosphorinan-1-yl)ethane                                                   | XAZZED      | photochemically induced oxidation⁵                 |

Table S6. Summary of the filtering statistics for the TMCs at each generation, including the number attempted, number of complexes with valid initial geometry (i.e., no ligand clashing), and the number of complexes with good geometry and $<S^2>$ (judged by our established protocols⁶⁻⁷) after converged geometry optimizations. Generations that explored the base complexes space are shaded in blue and those that explored the functionalized complexes are shaded in green.

| generation | attempted | valid initial geometry | converged, good geometry and $<S^2>$ |
|------------|-----------|------------------------|--------------------------------------|
| 0          | 2000      | 1822                   | 1470                                 |
| 1          | 200       | 188                    | 146                                  |
| 2          | 200       | 195                    | 157                                  |
| 3          | 200       | 188                    | 146                                  |
| 4          | 200       | 143                    | 91                                   |
| 5          | 200       | 184                    | 151                                  |
| 6          | 200       | 188                    | 150                                  |

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Table S7. Summary of 23 DFAs in the original work of Duan et al.\textsuperscript{8}, including the rungs on “Jacob’s ladder” of DFT, HF exchange fraction, LRC range-separation parameter (bohr\textsuperscript{-1}), MP2 correlation fraction, and whether empirical (i.e., D3) dispersion correction is included.

| DFA           | type       | exchange type | HF exchange type | HF exchange percentage | LRC RS parameter (bohr\textsuperscript{-1}) | MP2 correlation | D3 dispersion |
|---------------|------------|---------------|------------------|------------------------|---------------------------------------------|-----------------|---------------|
| BP86\textsuperscript{9-10} | GGA        | GGA           |                  |                        | --                                          | --              | no            |
| BLYP\textsuperscript{11-12} | GGA        | GGA           |                  |                        | --                                          | --              | no            |
| PBE\textsuperscript{13}     | GGA        | GGA           |                  |                        | --                                          | --              | no            |
| TPSS\textsuperscript{14}    | meta-GGA   | meta-GGA      |                  |                        | --                                          | --              | no            |
| SCAN\textsuperscript{15}    | meta-GGA   | meta-GGA      |                  |                        | --                                          | --              | no            |
| M06-L\textsuperscript{16}   | meta-GGA   | meta-GGA      |                  |                        | --                                          | --              | no            |
| MN15-L\textsuperscript{17}  | meta-GGA   | meta-GGA      |                  |                        | --                                          | --              | no            |
| B3LYP\textsuperscript{18-20}| GGA hybrid | GGA           |                  |                        | 0.200                                       | --              | no            |
| B3P86\textsuperscript{9,18} | GGA hybrid | GGA           |                  |                        | 0.200                                       | --              | no            |
| B3PW91\textsuperscript{18,21}| GGA hybrid | GGA           |                  |                        | 0.200                                       | --              | no            |
| PBE0\textsuperscript{22}    | GGA hybrid | GGA           |                  |                        | 0.250                                       | --              | no            |
| \(\omega\)B97X\textsuperscript{23} | RS hybrid | GGA           |                  |                        | 0.158                                       | 0.300           | no            |
| LRC-\(\omega\)PBEh\textsuperscript{24} | RS hybrid | GGA           |                  |                        | 0.200                                       | 0.200           | no            |
| TPSSh\textsuperscript{14}   | meta-GGA hybrid | meta-GGA |                  |                        | 0.100                                       | --              | no            |
| SCANo\textsuperscript{25}   | meta-GGA hybrid | meta-GGA |                  |                        | 0.250                                       | --              | no            |
| M06\textsuperscript{26}     | meta-GGA hybrid | meta-GGA |                  |                        | 0.270                                       | --              | no            |
| M06-2X\textsuperscript{26}  | meta-GGA hybrid | meta-GGA |                  |                        | 0.540                                       | --              | no            |
| MN15\textsuperscript{27}    | meta-GGA hybrid | meta-GGA |                  |                        | 0.440                                       | --              | no            |
| B2GP-PLYP\textsuperscript{28} | double hybrid | GGA        |                  |                        | 0.650                                       | --              | 0.360         | no            |
| PBE0-DH\textsuperscript{29} | double hybrid | GGA        |                  |                        | 0.500                                       | --              | 0.125         | no            |
| DSD-BLYP-D3BJ\textsuperscript{10} | double hybrid | GGA        |                  | 0.710                  | --                                          | 1.000           | yes           |
| DSD-PBEB95-D3BJ\textsuperscript{10} | double hybrid | GGA        |                  | 0.660                  | --                                          | 1.000           | yes           |
| DSD-PBEP6-D3BJ\textsuperscript{10} | double hybrid | GGA        |                  | 0.690                  | --                                          | 1.000           | yes           |
Table S8. Range of hyperparameters sampled for ANN models trained from scratch with Hyperopt. The lists in the architecture row can refer to one, two, or three hidden layers (i.e., the number of items in the list), and the number of nodes in each layer are given as elements of the list. The built-in Tree of Parzen Estimator algorithm in Hyperopt was used for the hyperparameter selection process.

| Architecture | [[128], [256], [512], [128, 128], [256, 256], [512, 512], [128, 128, 128], [256, 256, 256], [512, 512, 512]] |
|--------------|------------------------------------------------------------------------------------------|
| L2 regularization | [1e-6, 1]                                                                                     |
| Dropout rate | [0, 0.5]                                                                                     |
| Learning rate | [1e-6, 1e-3]                                                                                   |
| Beta1        | [0.75, 0.99]                                                                                   |
| Batch size   | [16, 32, 64, 128, 256, 512]                                                                     |

References

1. Zhu, Q.-Y.; Lu, W.; Zhang, Y.; Bian, G.-Q.; Gu, J.; Lin, X.-M.; Dai, J., Syntheses, Crystal Structures, and Optical Properties of Metal Complexes with 4',5'-Diaza-9'-(4,5-disubstituted-1,3-dithiol-2-ylidene)fluorene Ligands. *Eur. J. Inorg. Chem.* 2008, 2008 (2), 230-238.

2. Wang, Y.; Zhang, Y.; Zhu, D.; Ma, K.; Ni, H.; Tang, G., Synthesis, structural characterization and theoretical approach of the tri(2-(2,6-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) cobalt(II). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2015, 147, 31-42.

3. Groué, A.; Tranchier, J. P.; Rager, M. N.; Gontard, G.; Métiévier, R.; Buriez, O.; Khatyr, A.; Knorr, M.; Amouri, H., Cyclometalated Rhodium and Iridium Complexes Containing Masked Catecholates: Synthesis, Structure, Electrochemistry, and Luminescence Properties. *Inorganic Chemistry* 2022, 61 (12), 4909-4918.

4. Pursche, D.; Triller, M. U.; Slinn, C.; Reddig, N.; Rompel, A.; Krebs, B., Mimicking the reduced, oxidized and azide inhibited form of manganese superoxide dismutase by mononuclear Mn compounds utilizing tridentate ligands. *Inorganica Chimica Acta* 2004, 357 (6), 1695-1702.

5. Field, L. D.; Thomas, I. P.; Turner, P.; Hambley, T. W., Synthesis and Crystal Structures of [Fe(bpe6)<emph type="8">2</emph>]<emph type="7">Cl</emph> and [FeCl<emph type="8">2</emph>]<emph type="7"><emph type="8">2</emph></emph>](bpe6 = 1,2-Bis(phosphorinan-1-yl)ethane). *Australian Journal of Chemistry* 2000, 53 (7), 541-544.

6. Nandy, A.; Duan, C.; Janet, J. P.; Gugler, S.; Kulik, H. J., Strategies and Software for Machine Learning Accelerated Discovery in Transition Metal Chemistry. *Industrial & Engineering Chemistry Research* 2018, 57 (42), 13973-13986.

7. Duan, C.; Janet, J. P.; Liu, F.; Nandy, A.; Kulik, H. J., Learning from Failure: Predicting Electronic Structure Calculation Outcomes with Machine Learning Models. *Journal of Chemical Theory and Computation* 2019, 15 (4), 2331-2345.

8. Duan, C.; Chen, S.; Taylor, M. G.; Liu, F.; Kulik, H. J., Machine learning to tame divergent density functional approximations: a new path to consensus materials design principles. *Chem. Sci.* 2021, 12 (39), 13021-13036.

9. Perdew, J. P., Density-Functional Approximation for the Correlation-Energy of the Inhomogeneous Electron-Gas. *Phys. Rev. B* 1986, 33 (12), 8822-8824.
10.  Becke, A. D., Density-Functional Exchange-Energy Approximation with Correct Asymptotic-Behavior. *Physical Review A* **1988**, *38* (6), 3098-3100.
11.  Devlin, F. J.; Finley, J. W.; Stephens, P. J.; Frisch, M. J., Ab-Initio Calculation of Vibrational Absorption and Circular-Dichroism Spectra Using Density-Functional Force-Fields - a Comparison of Local, Nonlocal, and Hybrid Density Functionals. *Journal of Physical Chemistry* **1995**, *99* (46), 16883-16902.
12.  Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., Results Obtained with the Correlation-Energy Density Functionals of Becke and Lee, Yang and Parr. *Chemical Physics Letters* **1989**, *157* (3), 200-206.
13.  Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865-3868.
14.  Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E., Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91* (14), 146401.
15.  Sun, J. W.; Ruzsinszky, A.; Perdew, J. P., Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* **2015**, *115* (3), 036402.
16.  Zhao, Y.; Truhlar, D. G., A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125* (19), 194101.
17.  Yu, H. S.; He, X.; Truhlar, D. G., MN15-L: A New Local Exchange-Correlation Functional for Kohn-Sham Density Functional Theory with Broad Accuracy for Atoms, Molecules, and Solids. *J. Chem. Theory Comput.* **2016**, *12* (3), 1280-1293.
18.  Becke, A. D., Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648-5652.
19.  Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785--789.
20.  Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98* (45), 11623-11627.
21.  Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Atoms, Molecules, Solids, and Surfaces - Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992**, *46* (11), 6671-6687.
22.  Adamo, C.; Barone, V., Toward Reliable Density Functional Methods Without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110* (13), 6158-6170.
23.  Chai, J. D.; Head-Gordon, M., Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128* (8), 084106.
24.  Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M., A Long-Range-Corrected Density Functional That Performs Well for Both Ground-State Properties and Time-Dependent Density Functional Theory Excitation Energies, Including Charge-Transfer Excited States. *J. Chem. Phys.* **2009**, *130* (5), 054112.
25.  Hui, K.; Chai, J. D., SCAN-based Hybrid and Double-Hybrid Density Functionals From Models Without Fitted Parameters. *J. Chem. Phys.* **2016**, *144* (4), 044114.
26.  Zhao, Y.; Truhlar, D. G., The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class
27. Yu, H. Y. S.; He, X.; Li, S. H. L.; Truhlar, D. G., MN15: A Kohn-Sham Global-Hybrid Exchange-Correlation Density Functional With Broad Accuracy for Multi-Reference and Single-Reference Systems and Noncovalent Interactions. *Theor. Chem. Acc.* 2008, 120 (1-3), 215-241.

28. Karton, A.; Tarnopolsky, A.; Lamere, J. F.; Schatz, G. C.; Martin, J. M. L., Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical Kinetics. *Journal of Physical Chemistry A* 2008, 112 (50), 12868-12886.

29. Bremond, E.; Adamo, C., Seeking for Parameter-Free Double-Hybrid Functionals: The PBE0-DH Model. *J. Chem. Phys.* 2011, 135 (2), 024106.

30. Kozuch, S.; Martin, J. M. L., Spin-Component-Scaled Double Hybrids: An Extensive Search for the Best Fifth-Rung Functionals Blending DFT and Perturbation Theory. *Journal of Computational Chemistry* 2013, 34 (27), 2327-2344.

31. Bergstra, J.; Yamins, D.; Cox, D. D. In *Hyperopt: A Python Library for Optimizing the Hyperparameters of Machine Learning Algorithms*, Proceedings of the 12th Python in science conference, 2013; pp 13-20.