Supporting Information

Novel Helical Assembly of a Pt(II) Phenylbipyridine Complex Directed by Metal–Metal Interaction and Aggregation-Induced Circularly Polarized Emission

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General Information: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2, DMF, and triethylamine were obtained by distillation over CaH_2. ^1H and ^{13}C NMR spectra were recorded on a Varian mercury-300 spectrometer and JEOL JNM-ECA600 spectrometer at 25 ^oC in $CDCl_3$ and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 for ^1H and 77.3 for ^{13}C). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Fluorescence quantum yields were recorded on a JASCO FP-6500 spectrofluorometer with an integrating sphere (JASCO, ILF-533, diameter 10 cm). CD spectra were recorded on a JASCO J-720W spectropolarimeter. IR spectra were recorded on JASCO FT/IR-420S spectrometer. ESI-Mass spectra were recorded on Thermo Scientific LTQ Orbitrap XL hybrid FTMS. Optical rotations were recorded on a JASCO DIP-370 polarimeter. UV/vis absorption, fluorescence, and CD spectra were measured using a conventional quartz cell (light path 1 cm) with temperature control. Elemental analyses were performed using CHN analyzer. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. Compounds **2**,[1] *S*- and *R*-**3**,[1] and **5**[2] were prepared according to the reported methods.

Analysis of self-association by ^1H NMR experiments: Hyperbolic curves were obtained by plotting of compound concentrations vs ^1H NMR chemical shifts (δ) of the aromatic protons. The curve-fitting analysis of the plots was carried out on the basis of an isodesmic association model, which is a type of unlimited self-association where the addition of each successive monomer to polymer involves an equal association constant ($K_2 = K_3 = ... = K_i = K_E$). The fitting functions are given by equation 1 for NMR experiments. δ denotes apparent chemical shifts obtained from spectra; δ_m and δ_a are chemical shifts for a monomer and self-assembled species, respectively. K_E is the association constant; and c is the total concentration of a compound. The complexation-induced shift $\Delta\delta$ displays the difference between δ_m and δ_a.

$$\delta(c) = \delta_m + (\delta_a - \delta_m)\left(1 + \frac{1-\sqrt{4K_E c + 1}}{2K_E c}\right) \quad (1)$$

Determination of the CD dissymmetry factor g_{abs} and the CPL dissymmetry factor g_{lum}: The CD dissymmetry factors g_{abs} were defined as $2\Delta\varepsilon/\varepsilon$ at the wavelength of the first Cotton effect (468 nm). $\Delta\varepsilon$ and ε are the molar circular dichroism and the molar extinction coefficient, respectively.

The CPL dissymmetry factors g_{lum} were defined as $2\Delta I/I$ at the wavelength of the strongest CPL (530 nm). ΔI and I are the CPL and fluorescence intensities, respectively.

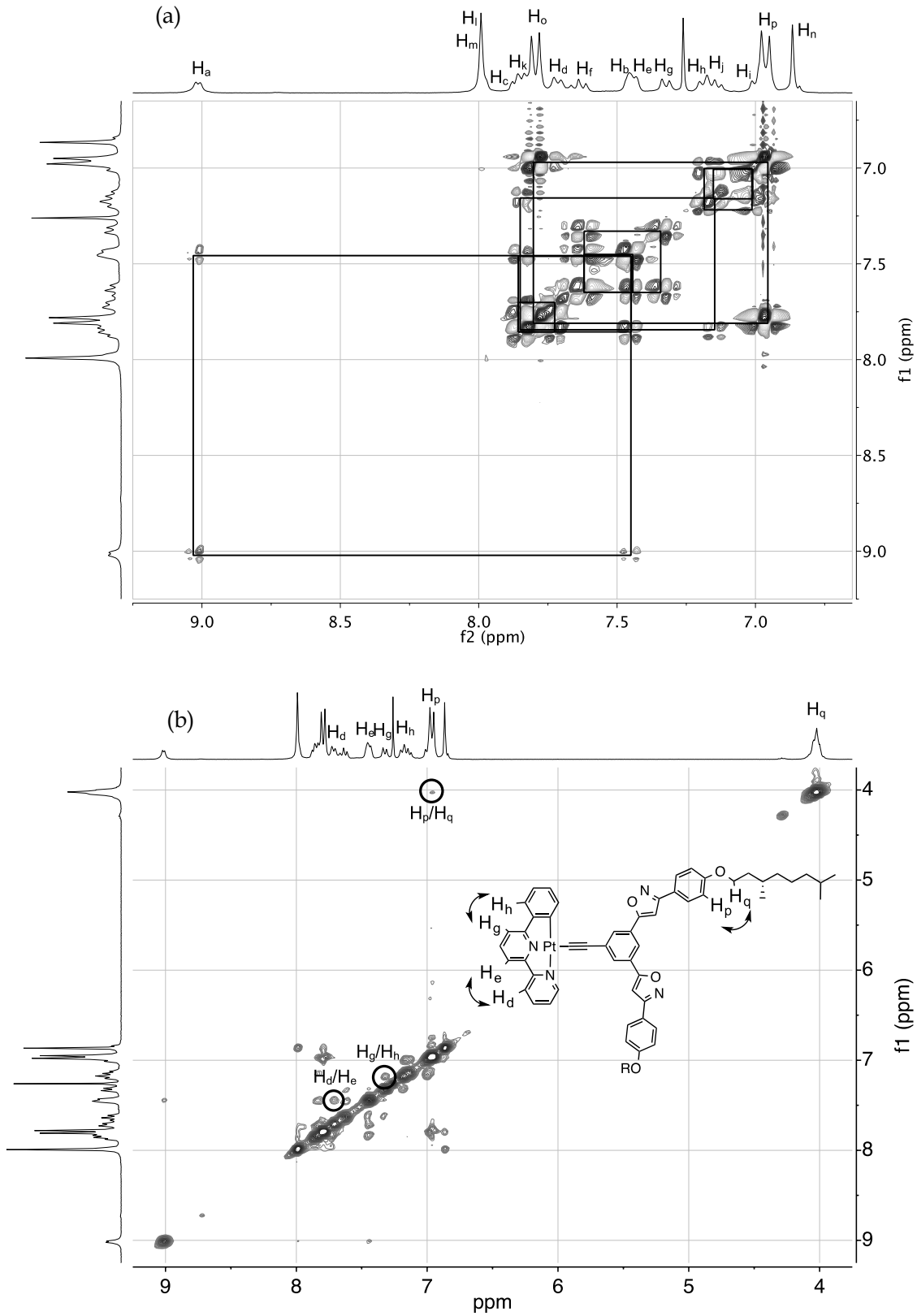


Figure S1. (a) COSY and (b) NOESY spectra of *S*-**1** at 298 K in chloroform-d_1.

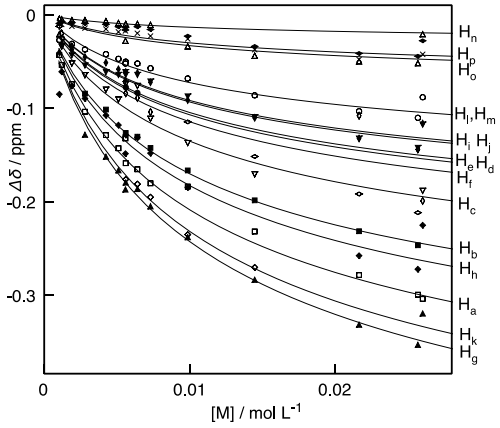


Figure S2. Non-linear curve fitting of *S*-**1** using ^{1}H NMR in chloroform-d_1 at 298 K. The solid curves were obtained by the fitting analysis.

Table S1. Aggregation-induced shifts of *S*-**1** in chloroform-d_1 at 298 K.

	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	H_k	H_l	H_m	H_n	H_o	H_p
$\Delta\delta$	–0.57	–0.56	–0.37	–0.29	–0.28	–0.31	–0.66	–0.50	–0.25	–0.25	–0.63	–0.20	–0.20	–0.04	–0.09	–0.08

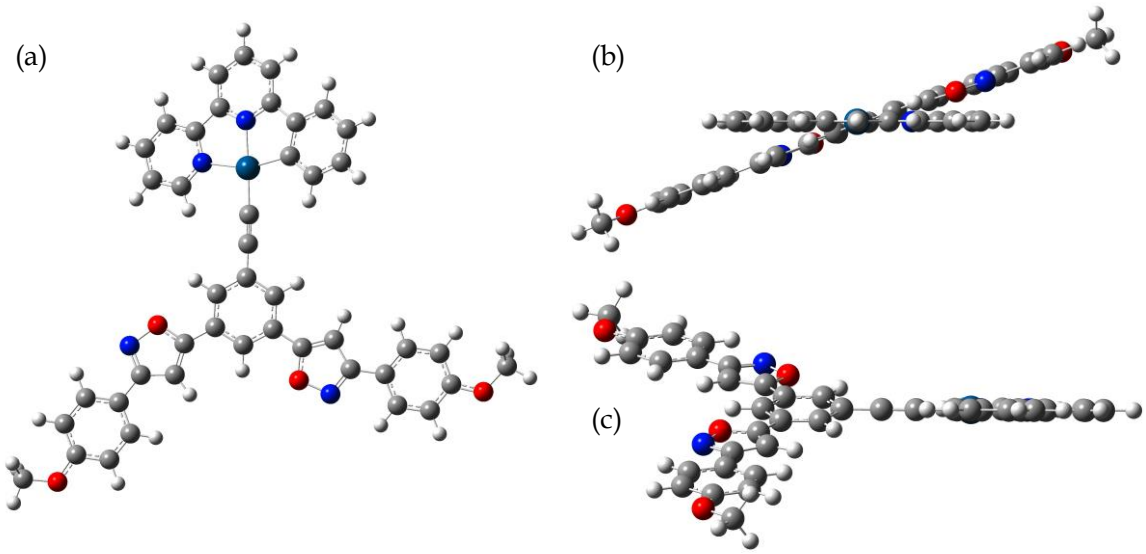


Figure S3. Energy minimized structure calculated by DFT method at B3LYP/LanL2DZ [Pt] + 6-31G(d) [C,H,N,O] level of Pt(II)phenylbipyridine complex possessing bis(*p*-methoxyphenylisoxazolyl)phenylacetylene ligand.[3] (a) Top view, (b), (c) side view. The chiral alkyl chains of *S*-**1** are replaced by methyl groups.

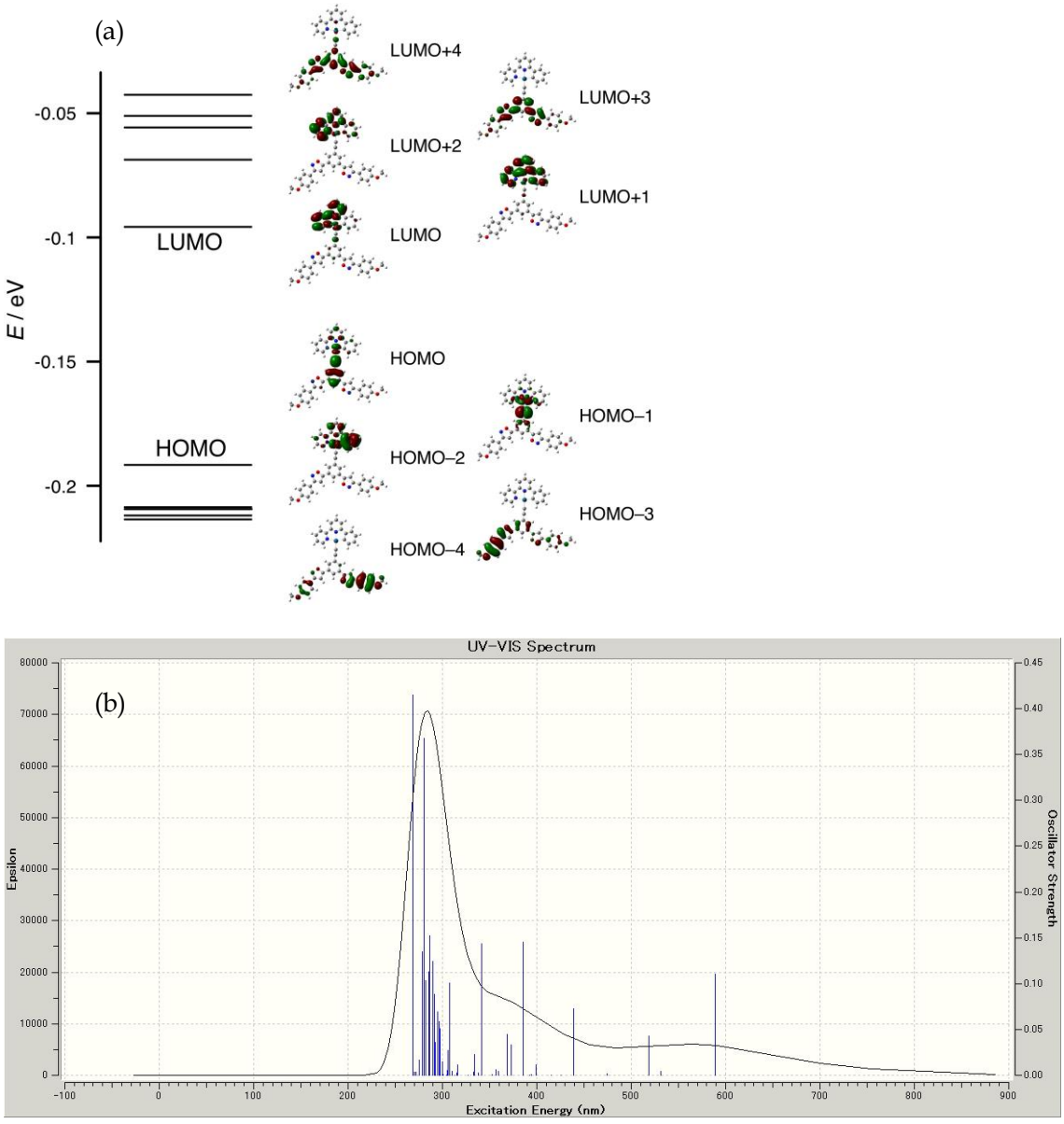


Figure S4. (a) Energy diagram of Pt(II)phenylbipyridine complex possessing bis(*p*-methoxyphenylisoxazolyl)phenylacetylene ligand calculated by TD-DFT at B3LYP/LanL2DZ [Pt] + 6-31+G(d,p) [C,H,N,O] level. (b) Calculated UV/vis absorption spectrum.

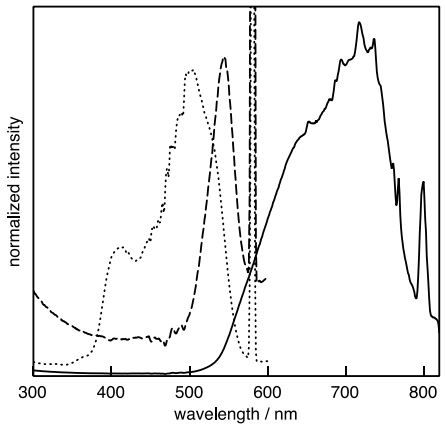


Figure S5. Excitation spectra of *S*-**1** in chloroform at 25 °C. The concentration of the solution of *S*-**1** are 0.49 (dotted line) and 5.17 (dashed and solid line) mmol L^{-1}. λ_{em} = 580 (dotted and dashed line) and 800 (solid line) nm.

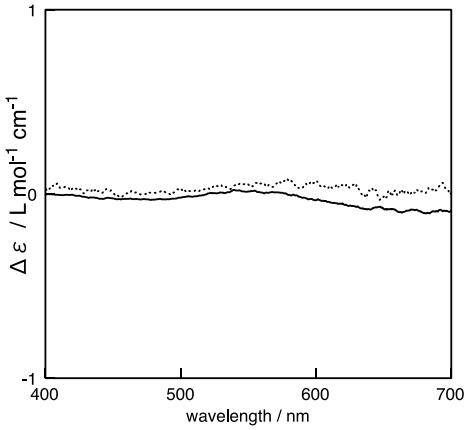


Figure S6. CD spectra of *S*-**1** in chloroform at 25 °C. The concentration of the solution of *S*-**1** are 0.49 (dotted line) and 5.17 (solid line) mmol L^{-1}.

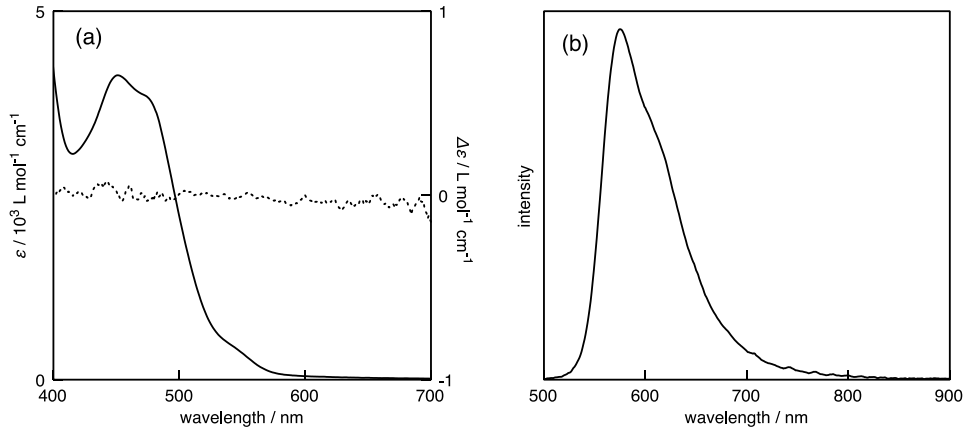


Figure S7. (a) UV/vis absorption (solid line) and CD (dotted line), and (b) emission spectra of *S*-**1** (0.50 mmol L^{-1}) in toluene at 50 °C. λ_{ex} = 444 nm.

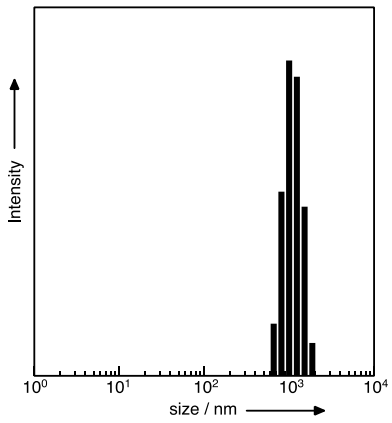


Figure S8. Dynamic light scattering (DLS) profile showing the intensity-averaged hydrodynamic radius of *S*-**1** in toluene at 25 °C.

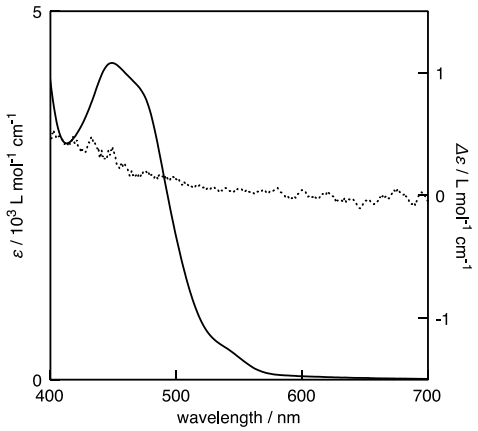


Figure S9. UV/vis absorption (solid line) and CD (dotted line) spectra of *S*-**1** (0.50 mmol L^{-1}) in toluene at 25 °C before heating.

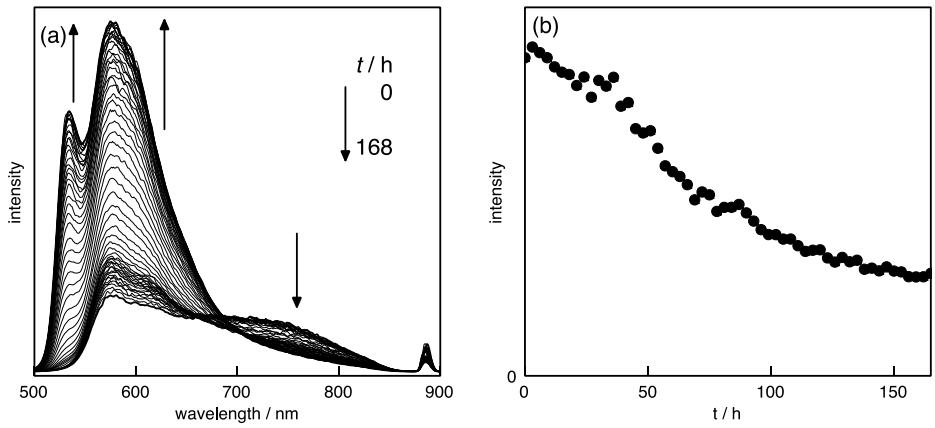


Figure S10. (a) Time-dependent emission spectra of *S*-**1** (0.50 mmol L^{-1}) in toluene at 25 °C before heating. (b) The plot of emission intensity at 820 nm vs *t*.

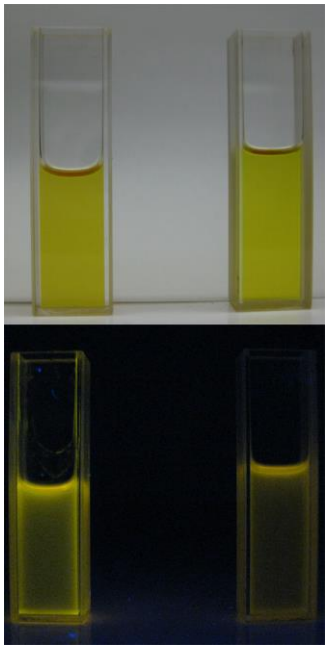


Figure S11. Photographs of (left) toluene solution and (right) chloroform solution of *S*-**1** under irradiation of (top) room light and (bottom) UV (365 nm) light.

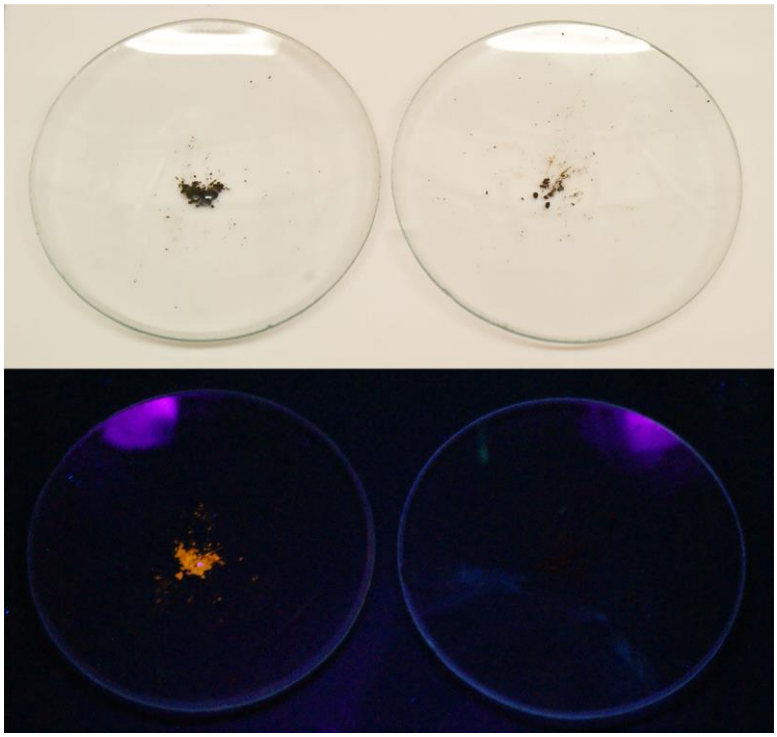


Figure S12. Photographs of solids of *S*-**1** obtained by evaporation of (left) toluene solution and (right) chloroform solution under irradiation of (top) room light and (bottom) UV (365 nm) light.

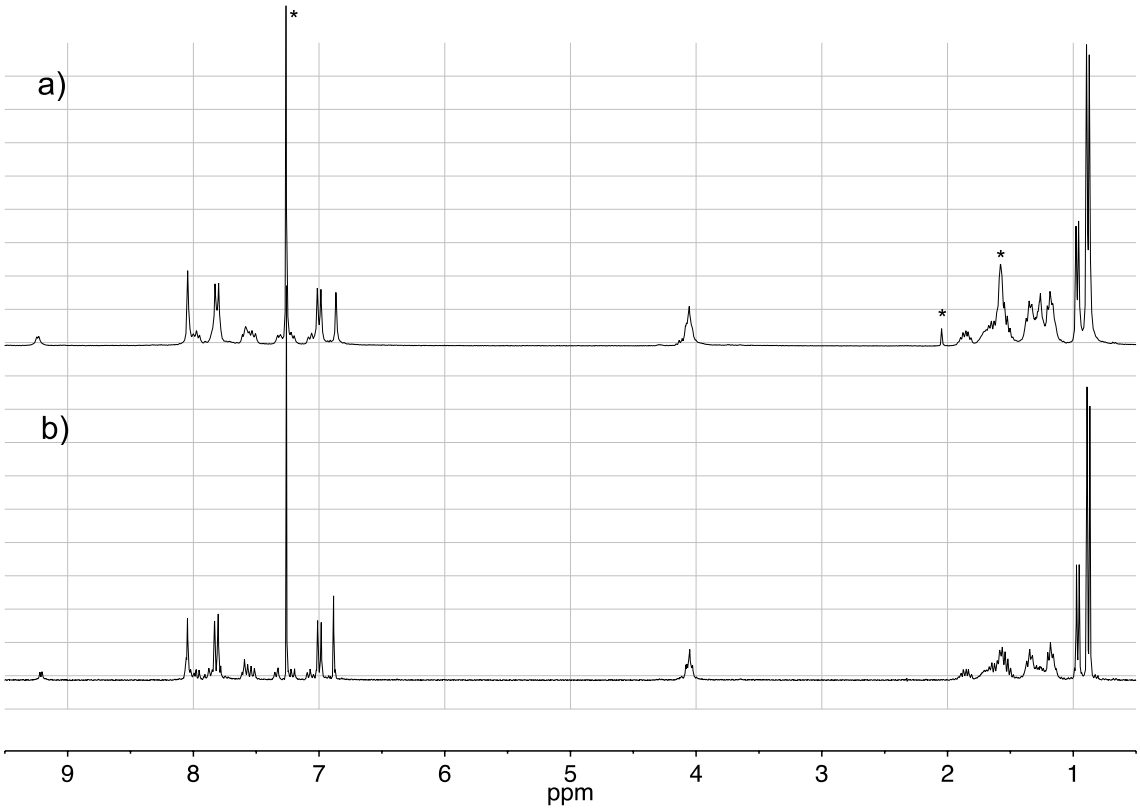


Figure S13. ^{1}H NMR spectra of (a) solid A and (b) solid B dissolved in chloroform-*d*. * indicates solvents and impurities.

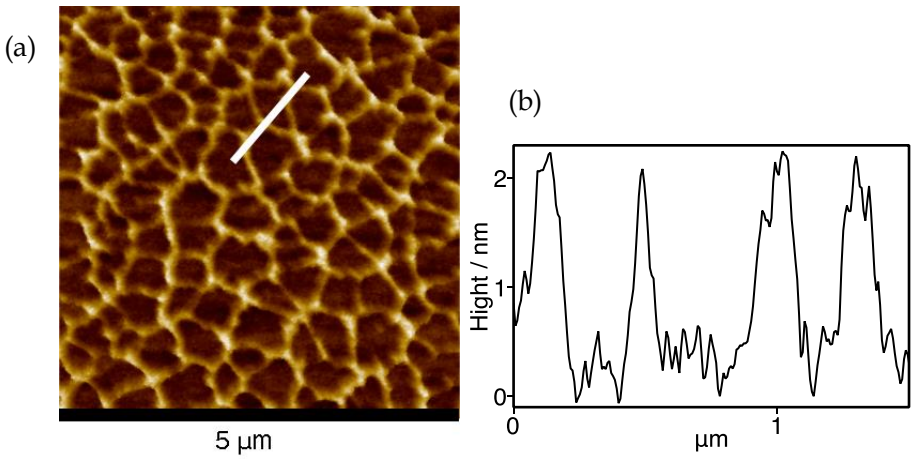


Figure S14. (a) AFM image of *S*-**1** on mica. The sample was prepared by spin-coating the toluene solution of *S*-**1** after one heating-cooling cycle. (b) Height profile on the white line of (a).

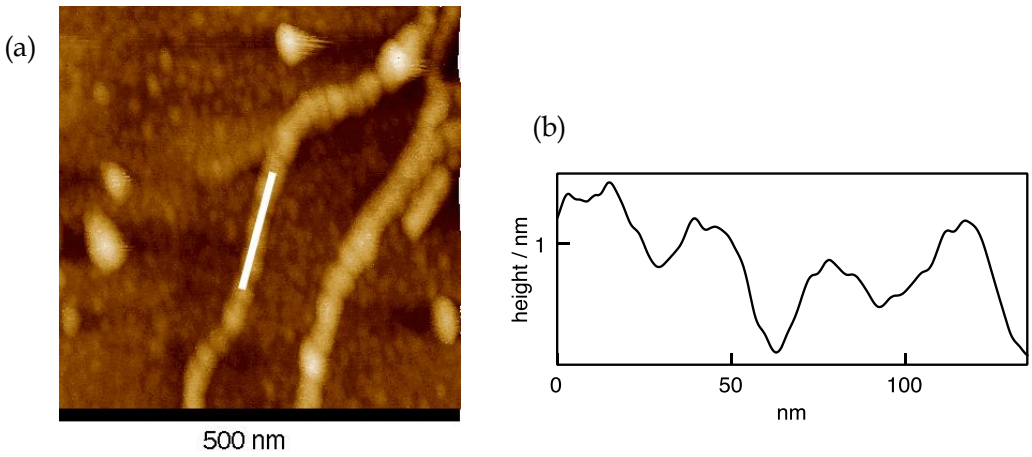


Figure S15. (a) AFM image of *S*-**1** on HOPG. The sample was prepared by spin-coating the toluene solution of *S*-**1** after one heating-cooling cycle. (b) Height profile on the white line of (a).

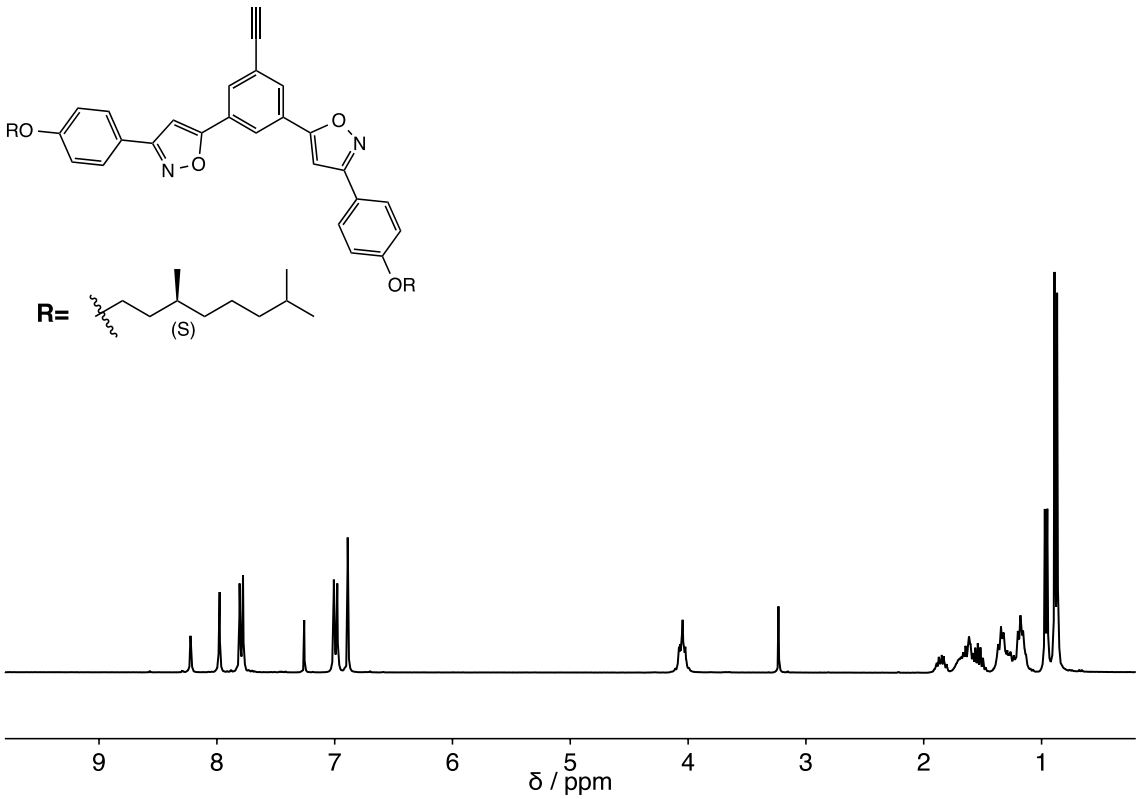
References

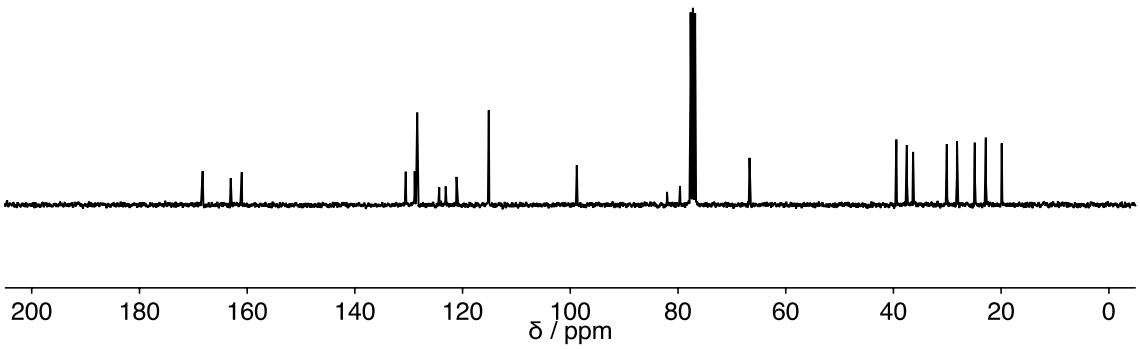
1) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi, and T. Haino, *J. Org. Chem.* **2011**, *76*, 5082.

2) X.-D. Du, J. Mo, X.-S. Li, Y.-S. Pan, and S.-M. Zhang, *Acta Cryst.* **2008**, *E64*, m1146.

3) Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

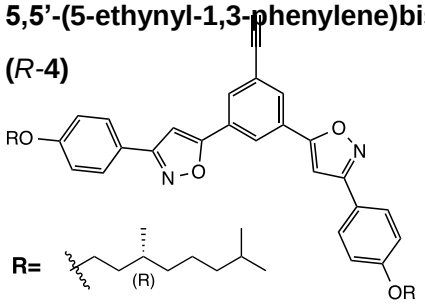
5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-((S)-3,7-dimethyloctyloxy)phenyl)isoxazole) (*S*-4)

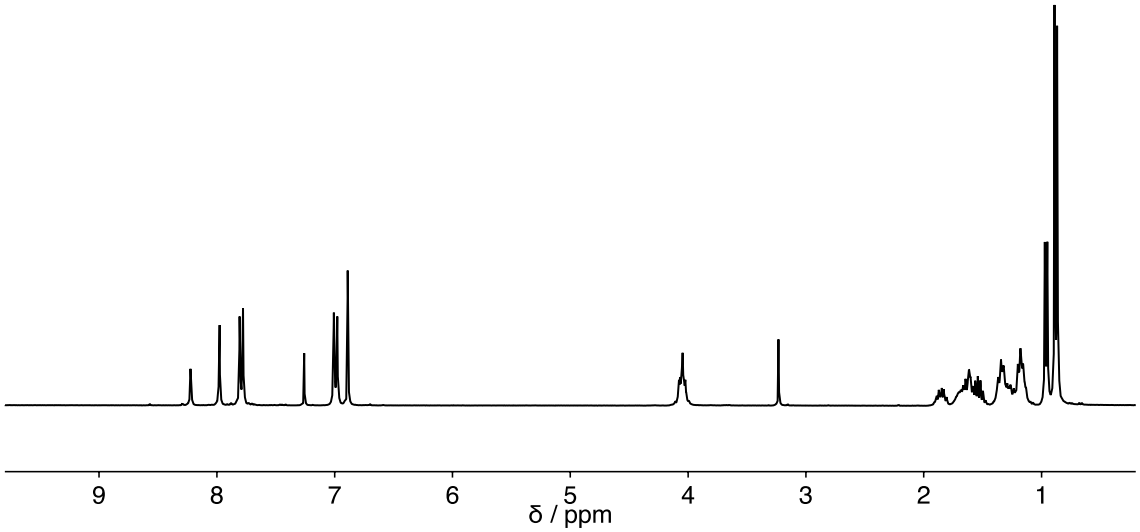


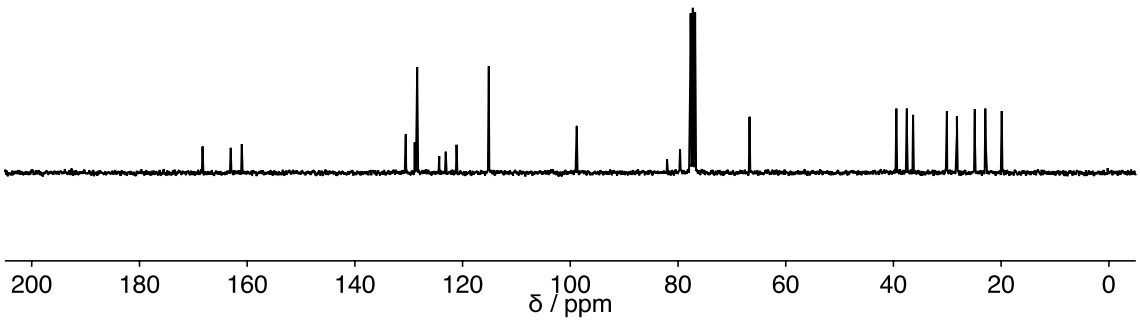


5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-((R)-3,7-dimethyloctyloxy)phenyl)isoxazole)

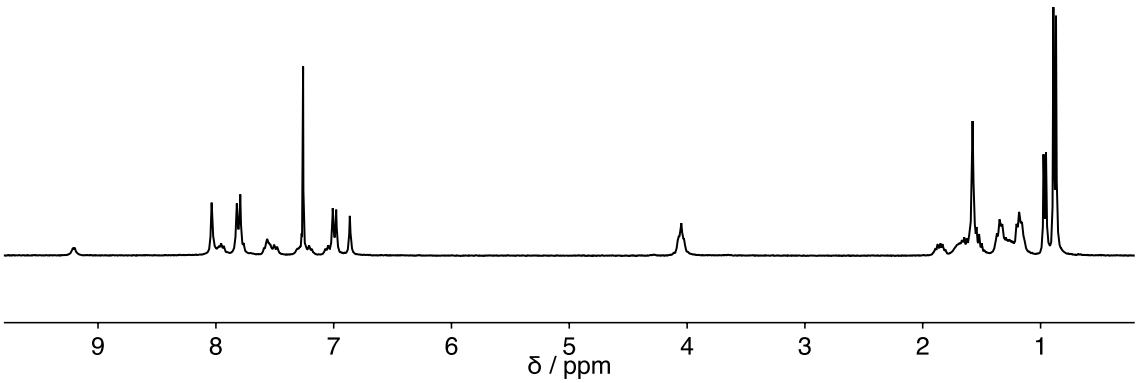
(*R*-4)

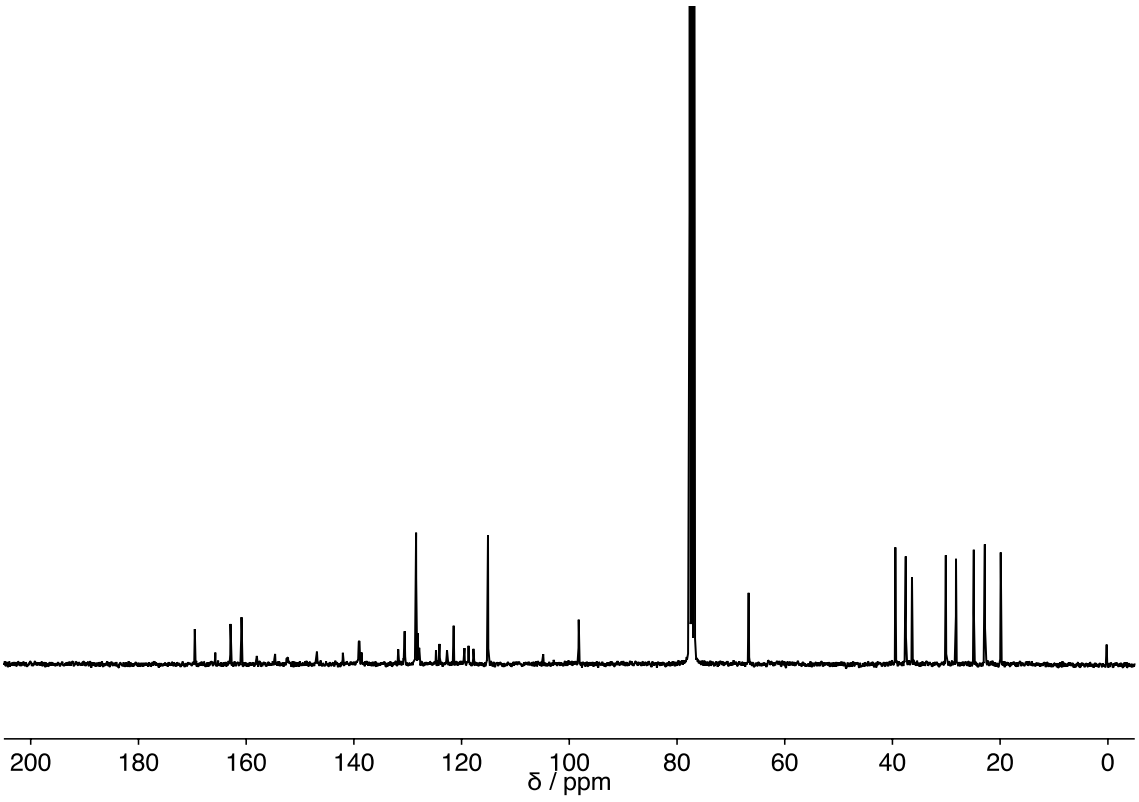




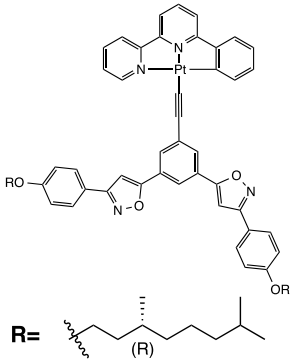


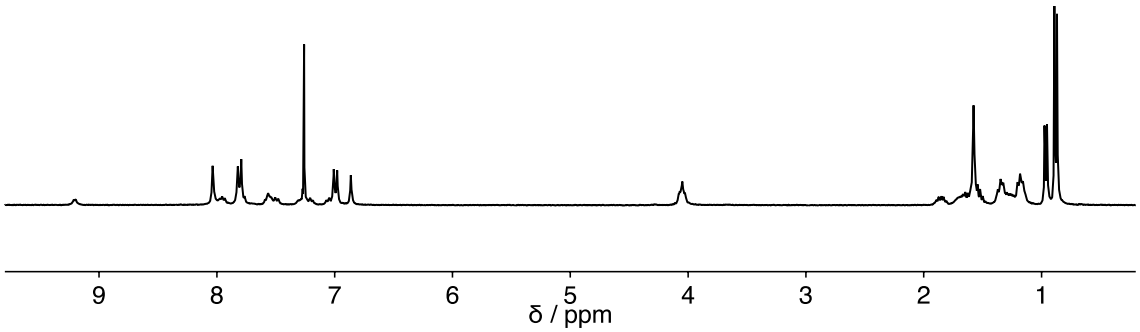
(6-phenyl-2,2'-bipyridine){5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-((S)-3,7-dimethyloctyloxy)phenyl)isoxazole)}platinum (*S*-1)

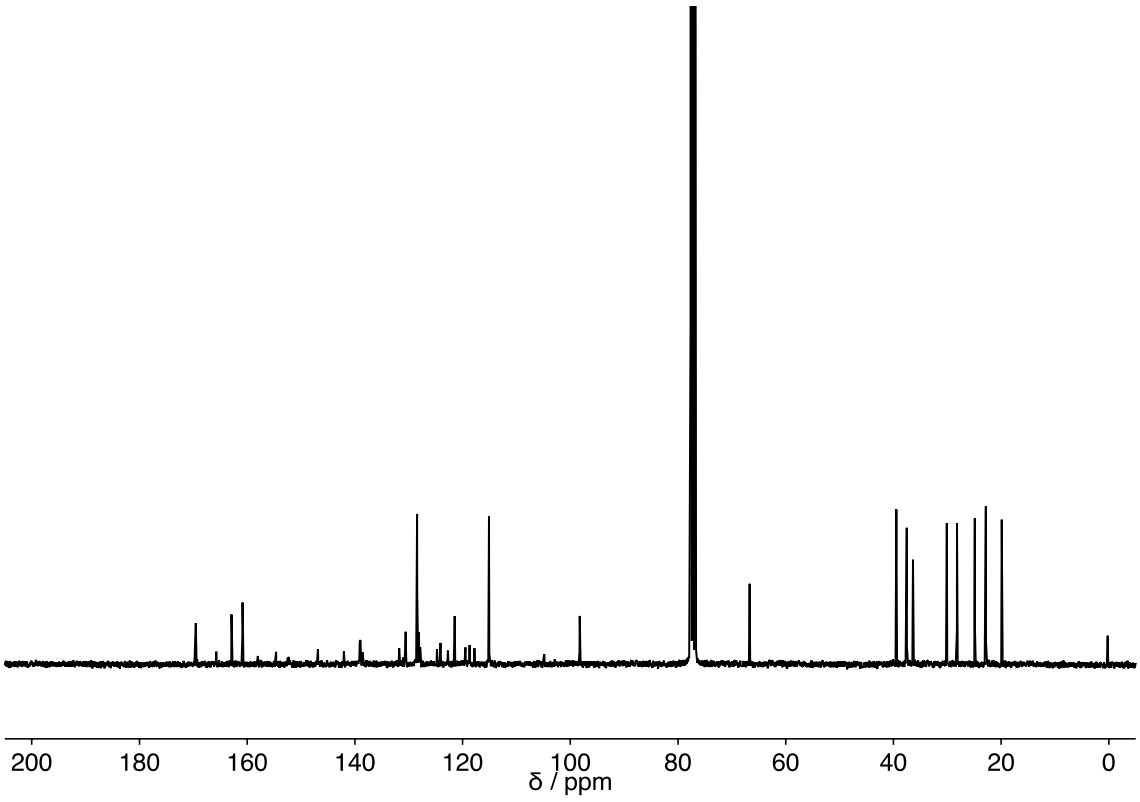




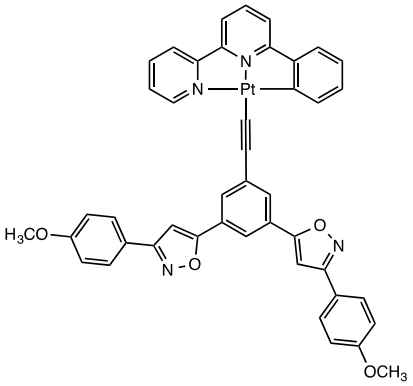
(6-phenyl-2,2'-bipyridine){5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-((R)-3,7-dimethyloctyl oxy)phenyl)isoxazole)}platinum (*R*-1)







Calculated Structure of Pt(II)phenylbipyridine complex possessing bis(*p*-methoxyphenylisoxazolyl)phenylacetylene ligand



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.590993	-3.263973	-0.394969
2	6	0	-6.248692	-2.870233	-0.372405
3	7	0	-5.932564	-1.603348	0.003266
4	6	0	-6.856367	-0.664609	0.370577
5	6	0	-8.211839	-1.033458	0.356700
6	6	0	-8.568571	-2.329431	-0.025836
7	6	0	-6.250481	0.621382	0.734085
8	6	0	-5.078827	-3.704376	-0.722988
9	6	0	-4.816903	0.696890	0.650709
10	6	0	-4.206961	1.911879	0.995870
11	6	0	-4.969683	3.012700	1.406730
12	6	0	-6.367482	2.927625	1.483021
13	6	0	-7.005546	1.733334	1.147068
14	6	0	-5.161479	-5.039996	-1.133162
15	6	0	-3.993310	-5.742867	-1.440338
16	6	0	-2.755971	-5.099192	-1.333579
17	6	0	-2.723805	-3.766513	-0.921201
18	7	0	-3.852509	-3.087591	-0.623654

19	78	0	-3.996532	-1.030887	0.037236
20	6	0	-2.098299	-0.510837	0.058568
21	6	0	-0.890681	-0.258320	0.049596
22	6	0	0.506749	0.016382	0.036059
23	6	0	0.987636	1.341738	-0.009921
24	6	0	2.365746	1.613462	-0.028913
25	6	0	3.285660	0.553425	0.000794
26	6	0	2.827615	-0.773538	0.049214
27	6	0	1.449031	-1.035263	0.065817
28	6	0	3.784734	-1.874733	0.080074
29	6	0	2.842654	2.991515	-0.083042
30	6	0	5.152068	-1.942914	0.131297
31	6	0	5.478155	-3.338488	0.141162
32	7	0	4.381066	-4.103562	0.097015
33	8	0	3.275283	-3.163477	0.057588
34	6	0	2.222965	4.211597	-0.143643
35	6	0	3.272960	5.187117	-0.177113
36	7	0	4.481678	4.614742	-0.139529
37	8	0	4.214468	3.189138	-0.078284
38	6	0	6.808177	-3.958763	0.195074
39	6	0	3.153403	6.648909	-0.246108
40	6	0	7.979693	-3.175256	0.180450
41	6	0	9.237273	-3.766749	0.231866
42	6	0	9.351669	-5.163402	0.299179
43	6	0	8.198435	-5.961470	0.314448
44	6	0	6.941456	-5.356808	0.262801
45	6	0	1.898618	7.274565	-0.288844
46	6	0	1.782417	8.666907	-0.356283
47	6	0	2.940657	9.453514	-0.381799
48	6	0	4.205906	8.843460	-0.339474
49	6	0	4.309171	7.461146	-0.272508
50	8	0	10.648497	-5.657845	0.346706
51	8	0	2.946093	10.840445	-0.448023

52	6	0	10.849978	-7.094316	0.414070
53	6	0	1.677724	11.545686	-0.491402
54	1	0	-7.875170	-4.265874	-0.689745
55	1	0	-8.973223	-0.318345	0.640762
56	1	0	-9.614126	-2.616852	-0.037351
57	1	0	-3.127410	1.989811	0.942377
58	1	0	-4.473132	3.942319	1.670544
59	1	0	-6.951671	3.784533	1.802436
60	1	0	-8.088719	1.671511	1.208566
61	1	0	-6.125801	-5.526548	-1.211079
62	1	0	-4.049854	-6.777976	-1.757805
63	1	0	-1.831414	-5.614697	-1.562883
64	1	0	-1.802792	-3.207159	-0.816331
65	1	0	0.268624	2.152374	-0.031795
66	1	0	4.345171	0.775115	-0.018604
67	1	0	1.100486	-2.059268	0.106092
68	1	0	5.840201	-1.116218	0.167521
69	1	0	1.163441	4.398903	-0.164819
70	1	0	7.911043	-2.094346	0.125633
71	1	0	10.142771	-3.172009	0.220461
72	1	0	8.265704	-7.041077	0.366901
73	1	0	6.047404	-5.969509	0.275962
74	1	0	0.992379	6.678688	-0.270396
75	1	0	0.797866	9.116557	-0.388312
76	1	0	5.085638	9.475615	-0.360371
77	1	0	5.283945	6.988820	-0.239982
78	1	0	11.930574	-7.228976	0.439478
79	1	0	10.434851	-7.595544	-0.468136
80	1	0	10.402859	-7.516503	1.321633
81	1	0	1.940585	12.601638	-0.539323
82	1	0	1.084538	11.352269	0.410125
83	1	0	1.098320	11.267758	-1.379735
