Supplementary Information

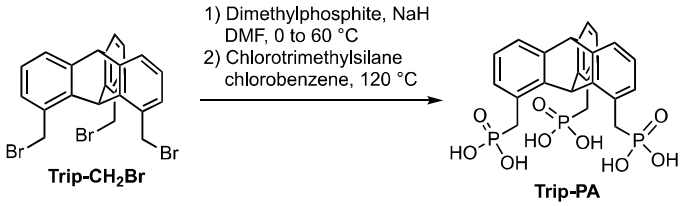
Phosphonic Acid Anchored Tripodal Molecular Films on Indium Tin Oxide

Chaoran Zhang,[1] Saunak Das,[1] Naoya Sakurai,[2] Takaki Imaizumi,[2] Sajisha Sanjayan,[2] Yoshiaki Shoji,[2] Takanori Fukushima,[2,3,*] and Michael Zharnikov[1*]

[1]*Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany*

[2] *Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

[3] *Living Systems Materialogy (LiSM) Research Group, International Research Frontiers Initiative (IRFI), Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8501, Japan*



1,8,13-Tris(bromomethyl)triptycene (**Trip-CH_2Br**) was prepared according to previously reported procedures.[1]

Synthesis of Trip-PA. Under nitrogen, an *N*,*N*-dimethylformamide (DMF) suspension (3.0 mL) of a mixture of dimethyl phosphite (173 μL, 1.69 mmol) and sodium hydride (41 mg, 1.69 mmol) were stirred at 25 °C for 1 h. To the mixture was added **Trip-CH_2Br** (150 mg, 0.281 mmol) at 0 °C, and the resulting mixture was stirred for 18 h at 60 °C. After allowed to cool to 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed successively with a saturated aqueous solution of NH_4Cl and brine, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. To the residue was added chlorobenzene (1.5 mL) and chlorotrimethylsilane (250 μL, 1.97 mmol), and the resulting mixture was stirred at 120 °C for 24 h and then allowed to cool to 25 °C. Water (1.0 mL) was added to the reaction mixture, and the white precipitate formed was collected by filtration, washed with cold water and hexane, and dried under reduced pressure. The residue was recrystallized from acetonitrile to give **Trip-PA** in 52% yield. FT-IR (KBr): ν (cm^{-1}) 3424, 2925, 2285, 1632, 1474, 1431, 1160, 999, 756, 539, 490. ^{1}H NMR (500 MHz, acetone-d_6, 25 °C): δ (ppm) 7.32 (d, J = 7.5 Hz, 3H), 7.10 (d, J = 7.5 Hz, 3H), 6.94 (dd, J = 7.5, 7.5 Hz, 3H), 6.59 (s, 1H), 5.56 (s, 1H), 3.82 (d, J = 21.5 Hz, 6H). ^{13}C NMR (126 MHz, acetone-d_6, 25 °C): δ (ppm) 147.3, 144.6, 129.5, 128.2, 125.4, 122.7, 56.1, 44.1, 32.5 (d, J = 133.9 Hz). ^{31}P NMR (202 MHz, acetone-d_6, 25 °C): δ (ppm) 25.3. ESI-TOF MS: calcd. for $C_{23}H_{23}O_9P_3$ $[M–H]^–$: m/z = 535.0471; found: 535.0499. The ^{1}H, ^{13}C, and ^{31}P NMR, and IR spectra of **Trip-PA** are shown in Figures S1, S2, S3, and S4, respectively.

Synthesis of NC-Trip-PA. This compound was obtained by a newly developed multistep procedure, with characterization of the synthetic intermediates at each stage. The detailed synthetic procedure will be reported elsewhere. FT-IR (KBr): ν(cm^{-1}) 3436, 2925, 2230, 1644, 1477, 1424, 1251, 1059, 942, 838, 803, 757, 556, 528. ^{1}H NMR (400 MHz, methanol-d_4, 25 °C): δ (ppm) 8.01 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.6 Hz, 3H), 7.16 (d, J = 7.8 Hz, 3H), 7.03 (dd, J = 7.8, 7.6 Hz, 3H), 6.39 (s, 1H), 3.59 (d, J = 20.7 Hz, 6H). ^{13}C NMR (126 MHz, methanol-d_4, 25 °C): δ (ppm) 146.1, 143.9, 133.8, 133.7, 129.9, 129.4, 128.8, 125.8, 121.6, 119.3, 113.5, 92.8, 90.2, 55.7, 43.4, 33.4, 32.2 (d, J = 135.3 Hz). ^{31}P NMR (202 MHz, methanol-d_4, 25 °C): δ (ppm) 24.1. ESI-TOF MS: calcd. for $C_{32}H_{25}NO_9P_3$ $[M–H]^–$: m/z = 660.0737; found: 660.0798. The ^{1}H, ^{13}C, and ^{31}P NMR, and IR spectra of **Trip-PA** are shown in Figures S5, S6, S7, and S8, respectively.

Analytical data

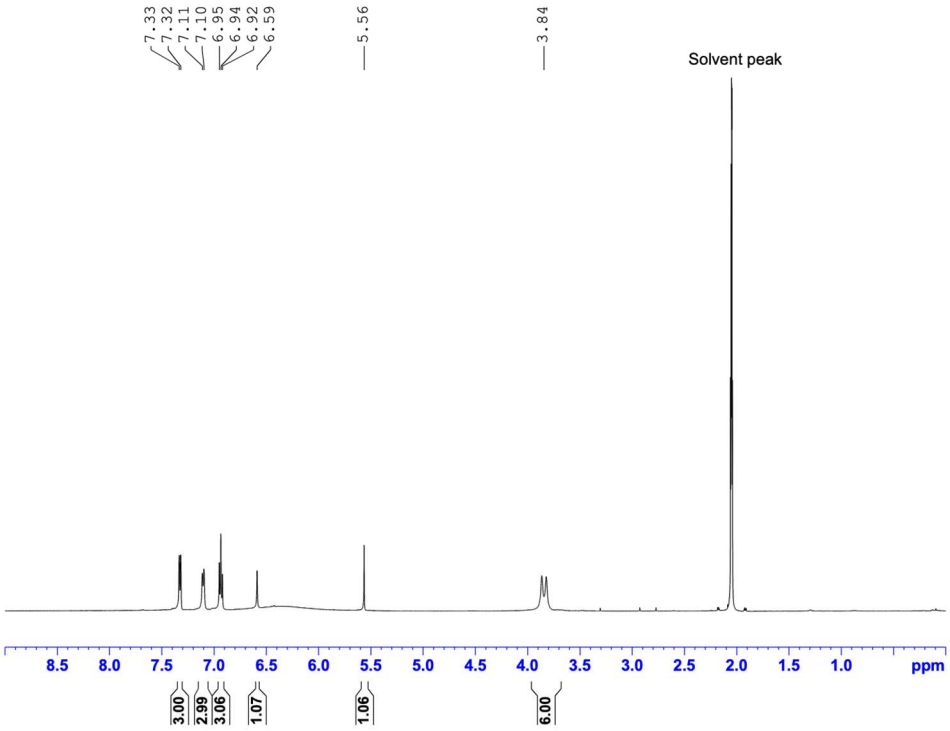


Figure S1. ^{1}H NMR spectrum (500 MHz) of **Trip-PA** in acetone-d_6 at 25 °C.

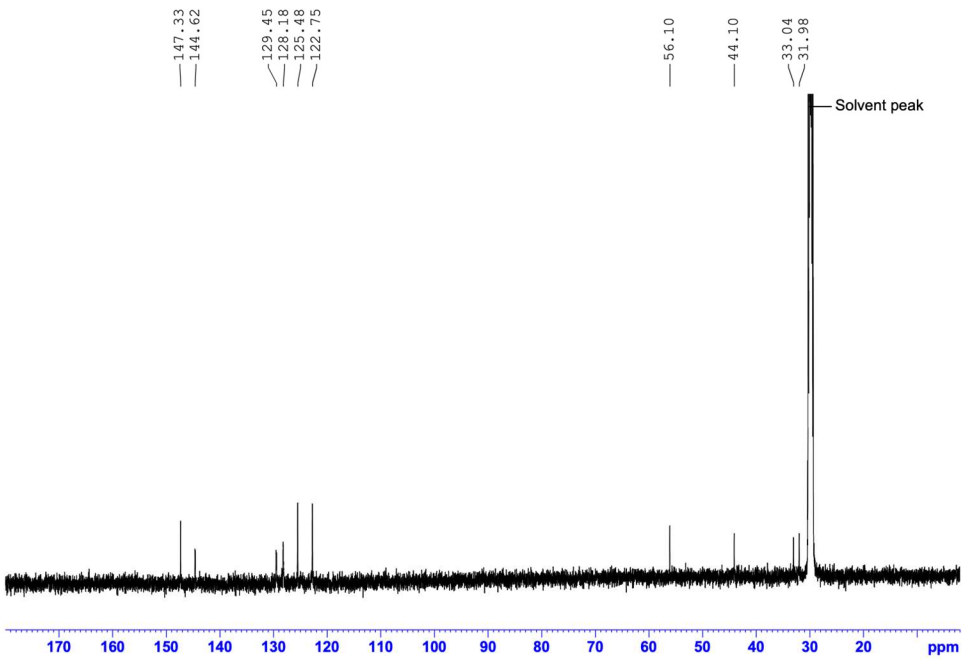


Figure S2. ^{13}C NMR spectrum (126 MHz) of **Trip-PA** in acetone-d_6 at 25 °C.

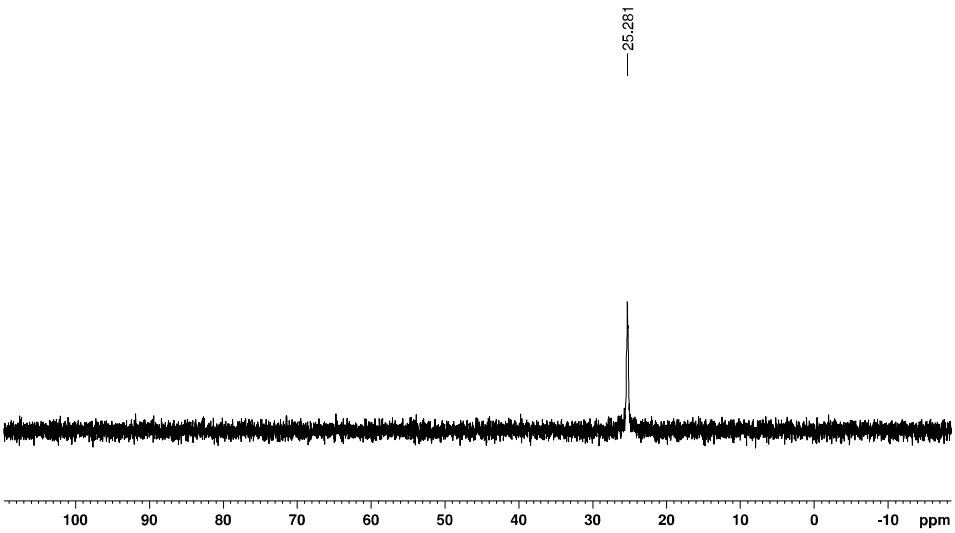


Figure S3. ^{31}P NMR spectrum (202 MHz) of **Trip-PA** in acetone-d_6 at 25 °C.

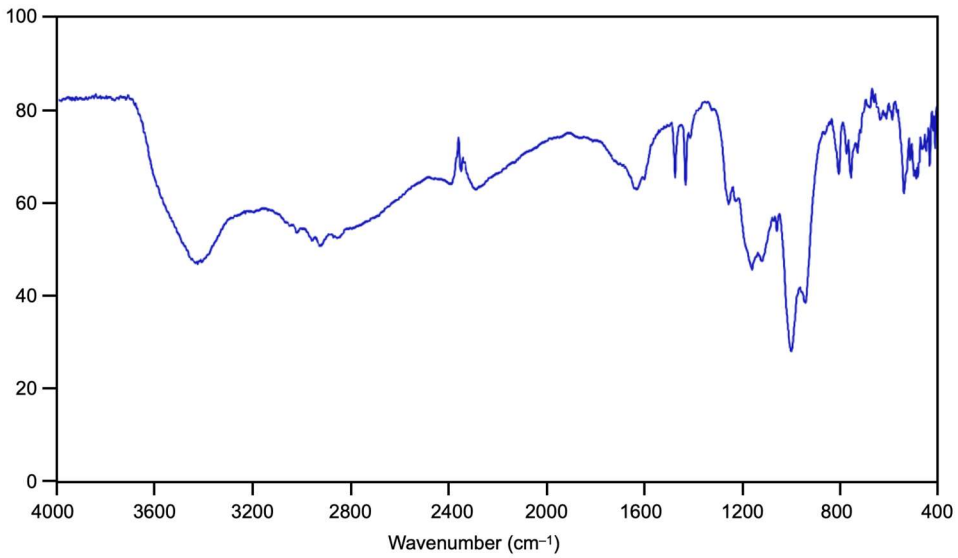


Figure S4. IR spectrum (KBr) of **Trip-PA** at 25 °C.

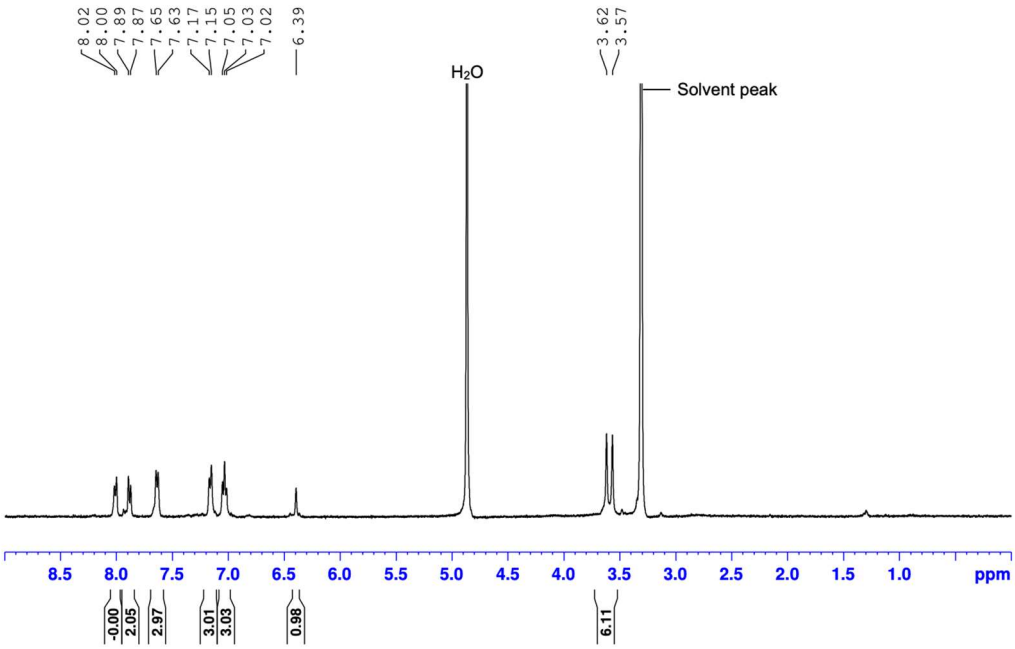


Figure S5. [1]H NMR spectrum (400 MHz) of **NC-Trip-PA** in mechanol-d_4 at 25 °C.

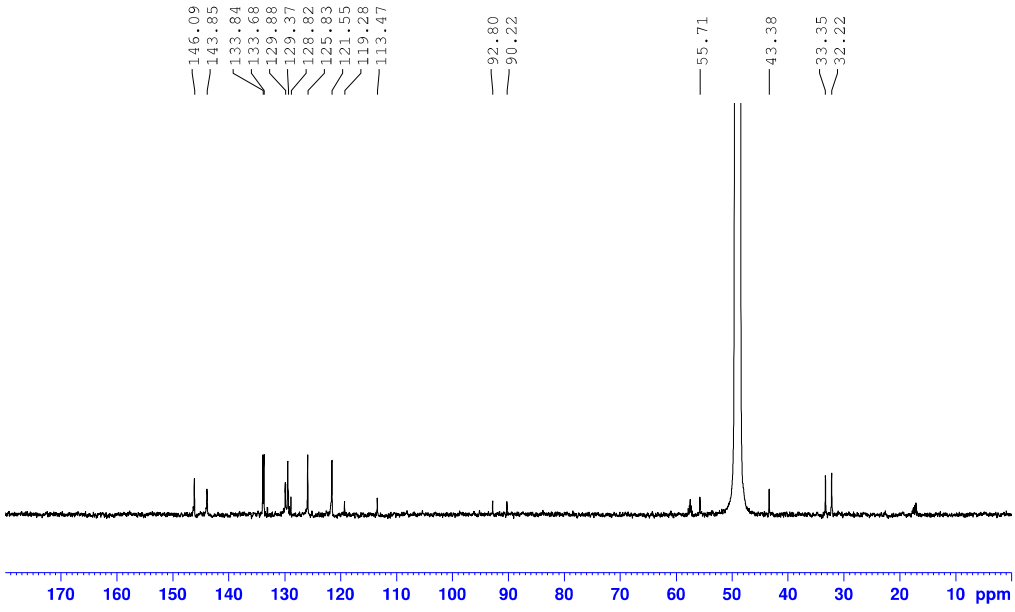


Figure S6. [13]C NMR spectrum (126 MHz) of **NC-Trip-PA** in methanol-d_4 at 25 °C.

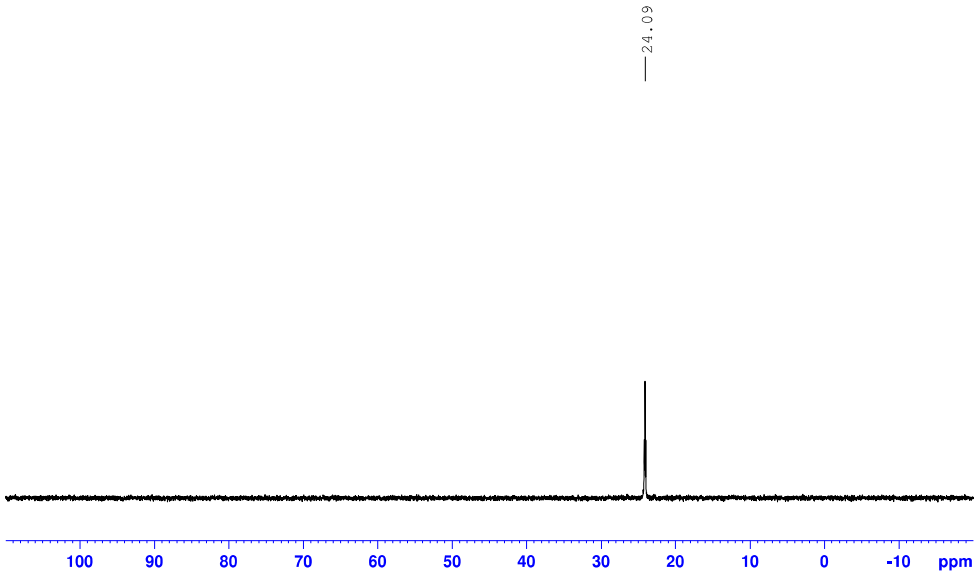


Figure S7. ^{31}P NMR spectrum (202 MHz) of **NC-Trip-PA** in methanol-d_4 at 25 °C.

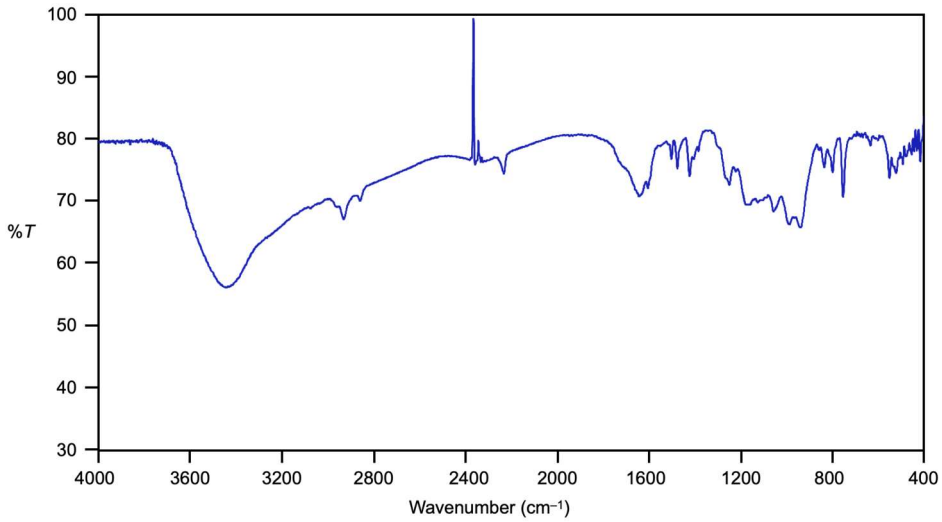


Figure S8. IR spectrum (KBr) of **NC-Trip-PA** at 25 °C.

References

1 Ishiwari, F.; Nascimbeni, G.; Sauter, E.; Tago, H.; Shoji, Y.; Fujii, S.; Kiguchi, M.; Tada, T.; Zharnikov, M.; Zojer, E.; Fukushima, T. *J. Am. Chem. Soc.* **2019**, *141*, 5995–6005.