Supplementary Information

Experimental Section:

Materials and methods.

All materials used for the synthesis of the nanocomposite dendrimers and model compounds were commercial products (Aldrich, Fluka, TCI, Strem, Acros, Avocado) and were used as received. All reactions were carried out using Schlenk techniques in an argon atmosphere with anhydrous solvents. The cyclometalled iridium chloro-bridged dimer [(ppy)2Ir(μ-Cl)2Ir(ppy)2] (where ppy=2-phenylpyridine) was prepared by a reported procedure.1

Instruments.

1H, 13C and 31P NMR data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to CDCl3 or CD2Cl2 (1H, 13C) and phosphoric acid (31P). MALDI-TOF mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as matrix and silver trifluoroacetate as ionizing salt when necessary. Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA 2050 module (heating rate of 10ºC min –1). UV-vis spectra were recorded on a Shimadzu model 2501-PC UV-VIS spectrometer and photoluminescence (PL) spectra were measured on a Perkin-Elmer (LS50B) spectrofluorimeter. The solution spectra were measured from dichloromethane solutions and the thin film spectra were recorded from thin films obtained by spin coating or drop casting on quartz glass plates.

Synthesis of hexa-(4-bromo-4'-biphenyloxy)cyclotriphosphazene (2)

The syntheses of the title compounds were accomplished following a modified literature procedure by reacting phosphonitrilic chloride trimer with 4-bromo-4'-hydroxy biphenyl respectively in the presence of K2CO3 in THF.2 A typical procedure for the synthesis of the hexabromobiphenyl compound 2 is as follows. A suspension of K2CO3 powder (6.68g, 48.3 mmol), 50 mL dry THF and 4-bromo-4'-hydroxy biphenyl (7.97g, 32 mmol) were stirred vigorously at 70°C for 3 h. A solution of phosphonitrilic chloride trimer (1.39g, 4.0 mmol) in 25 mL of dry THF was then added dropwise to the stirring suspension and allowed to react at 70°C for 48 h. The filtered THF solution was extracted with brine, and the organic layer was dried with MgSO4, filtered and concentrated on a rotary evaporator to obtain the crude product that was washed with methanol, dried and used without further purification for the next step. Yield 5.8 g (89 %). 1H NMR (CDCl3) δ = 6.98 (d, 12H, J = 8.8 Hz), 7.17 (d, 12H, J = 8.8 Hz), 7.24 (d, 12H, J = 8.8 Hz), 7.45 (d, 12H, J = 8.8 Hz); 13C NMR (CDCl3) δ = 121.49, 121.81 127.80, 128.28, 132.08, 136.72, 138.70, 150.27; 31P NMR (CDCl3) δ = 9.37; MS (MALDI): m/z 1624.00 (100 %). Calculated 100% m/z for C72H48Br6N3O6P3: 1622.78.

Synthesis of hexa-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-4'-biphenyloxy)-cyclotriphosphazene (3)

To a flame dried schlenk flask was added potassium acetate (1.77g, 18 mmol) and this was dried at 100°C for 45 min under vacuum. The flask was re-filled with argon and cooled to room temperature. Under a positive argon flow, (2) (1.62 g, 1.0 mmol), bispinacolatodiboron (2.28 g, 9.0 mmol), and palladium acetate (0.041 g, 0.18 mmol, 3 mol %) were added and subjected to three vacuum/argon cycles. Finally 20 mL of dry DMF was added and the reaction mixture was stirred at 80°C for 48 h. The reaction mixture was cooled and filtered through a short column packed with celite. The crude product was obtained by pouring the DMF solution into water, followed by filtration and vacuum drying. The crude product was again redissolved in DMF and filtered through a short column packed with MgSO4. The crude product was obtained from the
DMF solution through a second reprecipitation using water, filtered, dried and used without further purification for the next step. Yield > 85%. MS (MALDI): m/z 1907.37 (100%). Calculated 100% m/z for C_{108}H_{120}B_{6}N_{3}O_{18}P_{3}: 1904.84.

**Synthesis of di-(2-phenylpyridine)-(2-(3-bromophenyl)pyridine) iridium(III) (Ir(ppy)_2(Br-ppy) (4)**

Cyclometalled iridium chloro-bridged dimer [(ppy)_2Ir(μ-Cl)_2Ir(ppy)] (0.30 g, 0.39 mmol), 2-(3-bromophenyl)pyridine (0.26 g, 1.1 mmol) and silver triflate (0.17 g, 0.64 mmol) were added to a 50 mL schlenk flask. The flask was subjected to 3 vacuum/argon refill cycles followed by the addition of ethoxyethanol (3 mL) and stirred at 150°C for 3 days. The flask was cooled to room temperature and the contents precipitated into 50 mL of DI-water/5 mL methanol. The solids were filtered, washed with methanol and dried. The yellow powder was dissolved in 200 mL boiling THF, filtered quickly (removed some black solids), and rotovapped down to 10 mL. This mixture was poured into 50 mL 9:1 methanol:DI-water solution to produce a bright yellow powder. Yield 0.313 g (55%). MS (MALDI): m/z 733.30 (100%). Calculated 100% m/z for C_{33}H_{23}BrIrN_{3}: 733.07. Side products: m/z 813.26 (31%). Calculated 100% m/z for C_{33}H_{22}Br_{2}IrN_{3}: 812.98.

**Synthesis of compound (5)**

Compound (3) (0.52 g, 0.27 mmol), compound (4) (0.20 g, 0.27 mmol), and Pd(PPh_{3})_{4} (0.008g, 6.92 μmol) were added to a 50 mL schlenk flask. The flask was subjected to 3 vacuum/argon refill cycles followed by the addition of 20 mL dry DMF. This mixture was stirred until all materials had dissolved then a nitrogen degassed solution of 2M Na_{2}CO_{3} (0.27 mL, 0.54 mmol) was added and the reaction was stirred at 70°C for 3 hrs. 1-Bromonaphthalene was added (0.32 mL, 2.30 mmol) followed additional 2M Na_{2}CO_{3} (1.36 mL, 2.72 mmol), Pd(PPh_{3})_{4} (0.04g, 34.6 μmol) and 10 mL DMF and the reaction was stirred for 24 hrs at 90°C. The reaction was cooled to room temperature and poured into DI-water:methanol (3:1) to give an orange solid that was isolated by filtration. The dried powder was dissolved in CH_{2}Cl_{2} (50 mL) and filtered through a 0.2 μm membrane. The solution was reduced to ~10 mL and precipitated into methanol (containing 5% DI-water), filtered and dried. Finally the product was introduced onto a short silica column using minimal CH_{2}Cl_{2} followed by hexane:ethyl acetate (9:1) eluant and then CH_{2}Cl_{2}. The final orange-yellow solid was recovered by precipitation into methanol (5% DI-water) followed by filtration and vacuum drying. Yield 0.492 g (75%) MS (MALDI): m/z 2434.3. Calculated 100% m/z for C_{155}H_{106}IrN_{6}O_{6}P_{3}: 2433.7. (See Figure S4 for side products)

References

Figure S1. UV-vis spectrum in dichloromethane of Ir dendrimer (5).

Figure S2. Photoluminescent (PL) spectra of Ir dendrimer (5) as thin film (10 wt. % in poly(vinylcarbazole), PVK, and in solution (dichloromethane). Excitation wavelength for both was 378nm.
Figure S3. Thermal gravimetric analysis (TGA) plot in nitrogen of Ir dendrimer (5). Experiment run using 10°C/min ramp rate to 900°C. 5% weight loss occurs at 429°C.
Figure S4. MALDI-TOF of the target compound (5) and side products.