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Aromatic hydrocarbon macrocycles for highly efficient organic light-emitting devices with single-layer architectures †

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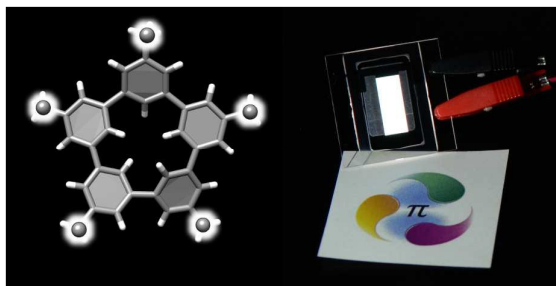
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ABSTRACT: A modern electrophosphorescent organic light-emitting device (OLED) achieves quantitative electro-optical conversion by using multiple molecular materials in layers designed through role allotment for independent and specific functions. A unique, potentially innovative device architecture, *i.e.*, single-layer phosphorescent OLED, is currently being developed by designing multirole base materials *via* a structural combination of multiple functional components in one molecule. The multirole molecules, however, inevitably require multiple processes to synthesize multiple components and, moreover, to assemble these components synthetically in one molecule. We herein show that the multirole base material for a highly efficient single-layer phosphorescent OLED can be designed and synthesized with a single, very simple aromatic hydrocarbon component of toluene merely through one-pot macrocyclization. Without passing the assembly tasks on the synthesis stage, the molecular design allows for a concise one-pot synthesis and for a quantitative electro-optical conversion in the single-layer device architecture with a single-component base material.

Introduction

An aromatic hydrocarbon, anthracene, was the first material to achieve direct-current electroluminescence.^{1,2} Although the discovery of the electroluminescence in this hydrocarbon marked the first, preliminary step toward an organic light-emitting device (OLED), the hydrocarbon molecule was replaced with heteroaromatic or organometallic molecules toward the development of the

state-of-the-art OLED with very high efficiency of electro-optical conversion. The deficiencies in thin-film devices of the hydrocarbon molecule, such as the faint luminescence and requirement of high voltage and low temperature, were thus overcome by the invention of a double-layer strategy.³ The double-layer strategy allotted the hole transport role to one molecule (arylamine) and the remaining roles to another molecule (organoaluminium), adopting a diode strategy with an electron rich, donor-type molecule for a hole-transport layer (HTL) and an electron deficient, acceptor-type molecule for an electron-transport layer (ETL). A further role allotment in OLED was elaborated by separation of a luminescence role with phosphorescent emitters to result in almost 100% internal quantum efficiency of electro-optical conversion and, as a result, an external quantum efficiency (EQE) of electroluminescence between 20% and 30%.⁴⁻⁷ The arrival of phosphorescent emitters, however, also necessitated further elaboration of molecular designs for multi-layer architectures, for instance, by using infirmly conjugated aromatic molecules with a high triplet-state energy (E_T) for a host in an emission layer (EML) and electronically-biased molecules with unbalanced charge mobilities for hole-blocking or electron-blocking layers (HBLs/EBLs) (Fig. 1a).^{8,9}

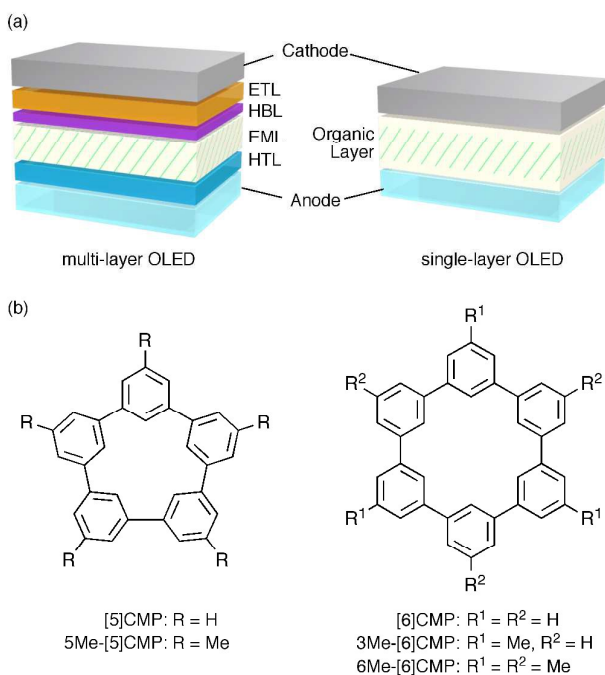


Fig. 1 Electrophosphorescent OLEDs. (a) Architectures of electrophosphorescent OLEDs in the present study. The multi-layer OLED with a four-layer architecture possesses the following layer settings: cathode = LiF (0.5 nm)/Al (100 nm), ETL = Alq₃ (20 nm), HBL = BAlq (10 nm), EML = 6 wt% Ir(ppy)₃ in a host material (40 nm), HTL = α -NPD (20 nm), anode = PEDOT:PSS (30 nm)/ITO (110 nm). The single-layer OLED with a simple architecture possesses the following layer settings: cathode = Cs (1.5 nm)/Al (100 nm), organic layer = base material (10 nm)/6 wt% Ir(ppy)₃ in base material (40 nm)/base material (10 nm), anode = PEDOT:PSS (30 nm)/ITO (110 nm). (b) Chemical structures of CMP. See Fig. S1 for chemical structures of other compounds.

A unique, potentially innovative architecture is currently being developed, *i.e.*, single-layer phosphorescent OLED (Fig. 1a).¹⁰⁻¹⁶ In the single-layer OLED, one base material is designed for multiple roles in the device and, with a phosphorescent emitter, can achieve nearly quantitative electro-optical conversion for the luminescence.¹⁰⁻¹² In principle, the single-layer OLED simplifies the device with the simple architecture and

dramatically reduces tasks at the layer assembly stage. However, the present molecular design of the base materials still relies on the conventional diode strategy and thus requires substantial efforts on the synthesis of multiple elemental components, such as donor or acceptor, and on the synthetic assembly thereof. Moreover, despite the synthetic efforts, the structural combination does not always succeed in the single-layer OLED with a high efficient luminescence,¹³⁻¹⁶ partly because a guiding principle for the successful synthetic assembly is yet to be uncovered.

Revisiting aromatic hydrocarbons, we recently introduced a macrocyclization strategy for OLED materials.¹⁷⁻²⁰ We demonstrated that electronically unbiased structures of hydrocarbons function as bipolar carrier transport materials for both electrons and holes. We envisioned that the bipolar characteristics of the aromatic hydrocarbons could be further developed into the multirole base materials in the single-layer OLED. We herein report our first effort on the design and synthesis of the multirole base materials of aromatic hydrocarbon macrocycles. A structure-performance relationship study revealed a particular importance of steric design in the hydrocarbon materials. Expectedly, the steric design at the periphery was essential to control the packing structures in devices, but, unexpectedly, the steric design at the macrocyclic core was also effective to preferably tweak the charge carrier mobility. As a result, one simple structural component of a hydrocarbon, *i.e.*, toluene, was transformed into the single-component, multirole base material for the single-layer OLED with an utmost efficiency of electro-optical conversion. Furthermore, the versatility of the hydrocarbon base material was also demonstrated by its applicability to a white-light emitting OLED

with three phosphorescent emitters. This study showed that the molecular design for the highly efficient single-layer OLED can depart from the conventional diode strategy and look more deeply into the wide bandgap structures of hydrocarbons, the very first origin of electroluminescent materials.¹

Results and discussion

Molecular design for multirole materials in OLED. We started the molecular design of aromatic hydrocarbon macrocycles from a screening study for the host materials in the EML. A remaining requisite for the aromatic hydrocarbon macrocycles as a multirole base material in the single-layer OLED was the applicability to host materials,^{17,18} which required a detour in the molecular design. Possessing electronically unbiased structures composed solely of hydrogen and carbon atoms, aromatic hydrocarbon macrocycles provide interesting and unique structural motifs that bear high thermal robustness and intrinsic bipolar charge transport abilities. Considering its smallest arylene units of benzene rings, we expected that [*n*]cyclo-*meta*-phenylene ([*n*]CMP; Fig. 1b) should also function as the host material for phosphorescent emitters. However, although [*n*]CMP indeed worked as bipolar charge transport materials both for the HTL and ETL with emission characteristics expected for the multi-layer phosphorescent device (Fig. 2),¹⁸ their performance as host materials in a typical multi-layer OLED was unexpectedly poor (Table 1). Thus, in an electrophosphorescent device using 6 wt% Ir(ppy)₃ as the doped emitter (see also Fig. 1a), [5]- and [6]CMP exhibited negligible luminescence with EQE values of 0.0% (driving voltage (DV) =

3.1 V) and 1.0% (DV = 4.0 V), respectively, which are far inferior to the EQE value of 4.9% (DV = 5.2 V) with the standard material 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP). Throughout this study, all the organic thin films in the devices were deposited through sublimation, and the representative EQE values after calibration with the angular distribution of the light were sampled at $0.1 \text{ mA}\cdot\text{cm}^{-2}$ for comparison. Other convertible measures of device performances, such as power efficiencies (PE) and current efficiencies (CE),⁹ are also shown as a reference.

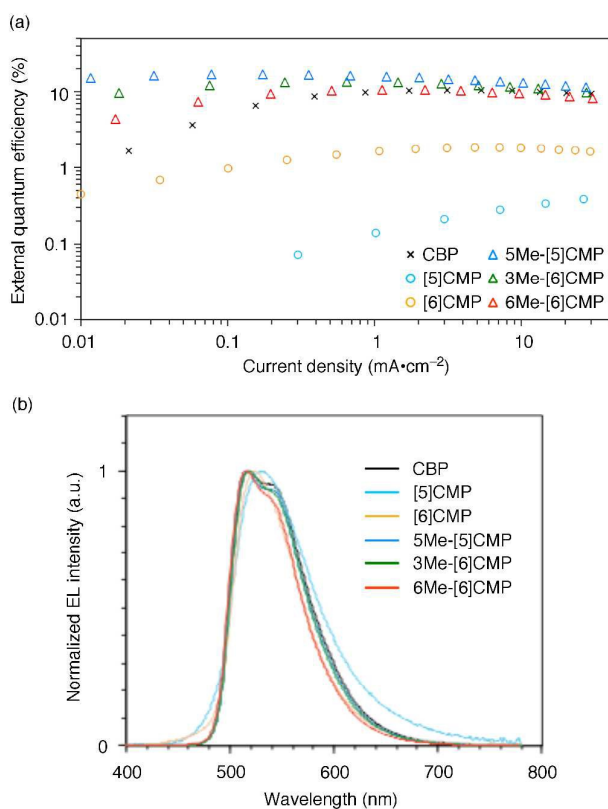


Fig. 2 Performance of multi-layer OLED with various hosts. (a) External quantum efficiency plotted as a function of current density. See Fig. 1a for the device architecture. (b) Electroluminescence spectra at a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$.

Table 1 Representative performance data of multi-layer phosphorescent OLED ^a

host material	EQE (%)	CE (cd•A ⁻¹)	PE (lm•W ⁻¹)	DV (V)
CBP	4.9	17.7	10.2	5.2
[5]CMP	0.0	0.0	0.0	3.1
[6]CMP	1.0	3.7	2.5	4.0
5Me-[5]CMP	16.8	55.1	31.2	6.1
3Me-[6]CMP	12.3	43.1	27.5	5.1
6Me-[6]CMP	7.9	29.2	15.6	5.6

^a Performances were evaluated at 0.1 mA•cm⁻², and the Lambertian factors for data calibrations were as follows. For EQE: CBP = 0.99, [5]CMP = 1.18, [6]CMP = 0.91, 5Me-[5]CMP = 1.10, 3Me-[6]CMP = 1.04 and 6Me-[6]CMP = 0.99. For PE: CBP = 0.97, [5]CMP = 1.04, [6]CMP = 0.84, 5Me-[5]CMP = 1.10, 3Me-[6]CMP = 1.03 and 6Me-[6]CMP = 0.96.

The molecular structures of CMP for the host materials were revised by taking account of relevant physical properties. Although the poor performance of [n]CMP as the host in OLED implied the leakage of the triplet-state excited energy of the Ir complex (*vide supra*), the solution-phase analysis of [n]CMP contrarily suggested their inherent potentials. Thus, the excited-state energy levels (E_S and E_T) for the singlet state (S_1) and triplet state (T_1) of [n]CMP in solution were high enough to accommodate the triplet-state energy of Ir(ppy)₃ (2.4 eV) (Table 2).²¹ We therefore hypothesized that crystalline characters in the deposited films resulted in the reduction of the excited-state energies of CMP.²² Theoretical calculations using the density functional theory (DFT) method indeed confirmed that the excited state energy (E_S) of [6]CMP could be reduced by approximately 0.4 eV upon crystallization (Fig. 3). The introduction of methyl (Me) groups at the periphery of [n]CMP was thus conceived to insulate the molecules from

the π -orbital overlaps for high- E_T host molecules, and a series of methylated congeners, $m\text{Me-}[n]\text{CMP}$ (Fig. 1b), were designed by adopting concise synthesis methods. In short, 5Me-[5]CMP and 6Me-[6]CMP were synthesized from 3,5-dibromotoluene through our one-pot, Ni-mediated macrocyclization method,^{18,23} and 3Me-[6]CMP was synthesized via a newly developed cross-macrocyclization method with Suzuki-Miyaura coupling reaction (Scheme 1) (see the Experimental Section for further details).²⁴

Table 2 Representative physical properties of CMPs

	T_d (°C) ^a	E_S (eV) ^b	E_T (eV) ^c
[5]CMP	358 ^d	3.52	2.73
[6]CMP	451 ^d	3.63	2.95
5Me-[5]CMP	369	3.53	2.68
3Me-[6]CMP	428	3.58	2.78
6Me-[6]CMP	433	3.63	2.77

^a The onset decomposition temperature T_d was determined by thermogravimetric analysis on a TG-DTA2500 (Netzsch) after an equilibration time of 10 min at 40 °C with a heating rate of 10 °C•min⁻¹ in flowing helium. ^b The E_S values were obtained from fluorescence spectra in chloroform at ambient temperature. ^c The E_T values were obtained from phosphorescence spectra with excitation at the absorption maximum in 2-methyltetrahydrofuran at 77 K. ^d The data were acquired from a previous report.¹⁸

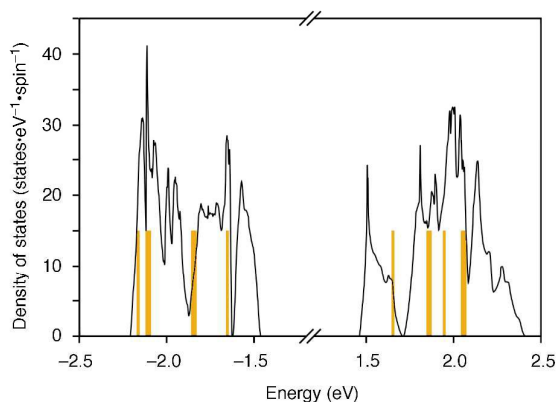
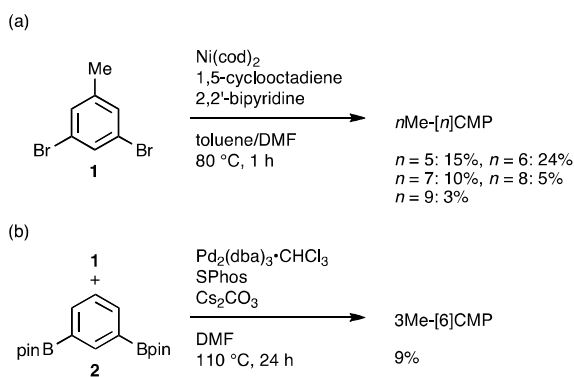


Fig. 3 DFT calculations of [6]CMP. Density of states of [6]CMP crystal (black lines) and the energy levels of isolated [6]CMP molecule (orange lines). The energy differences between the valence top state and the conduction bottom state are 2.92 eV for [6]CMP crystal and 3.30 eV for the [6]CMP molecule. The midgap energies are set to zero.



Scheme 1. Synthesis of *m*Me-[*n*]CMP. (a) Synthesis of *n*Me-[*n*]CMP (*n* = 5-9) via Yamamoto-type coupling reaction. (b) Synthesis of 3Me-[6]CMP via Suzuki-Miyaura cross-coupling reaction.

All three methylated congeners possessed preferable characteristics such as high- T_d and high- E_T values (Table 2) and worked well as the host material in the multi-layer OLED with Ir(ppy)₃ emitter. Thus, the EQE values were dramatically improved to 16.8% (DV = 6.1 V), 12.3% (DV = 5.1 V) and 7.9% (DV = 5.6 V) for

5Me-[5]CMP, 3Me-[6]CMP and 6Me-[6]CMP, respectively (Fig. 2 and Table 1). All of the EQE values were superior to the value of 4.9% ($DV = 5.2$ V) with CBP. The photoluminescence decay of Ir(ppy)₃ in *m*Me-[*n*]CMP layers confirmed a minute or negligible energy leakage in the thin films of these methylated hosts, and the comparison with those of unsubstituted CMP molecules clearly showed effective and favorable roles of the methyl groups for the exciton confinement (Fig. 4a). Atomic-force microscopy (AFM) analysis supported our hypothesis of the crystalline characters of unsubstituted congeners in thin films: the image of the [5]CMP film showed the presence of grains that were separated by boundaries of approximately 120-nm height,²⁵ whereas the image of the 5Me-[5]CMP film revealed the presence of a smooth surface with a maximum deviation of 3 nm in height (Fig. 4b). The surface roughness was evaluated, and average R_a values of 18.5 nm for [5]CMP and 0.5 nm for 5Me-[5]CMP were obtained, which indicated the formation of an amorphous film with 5Me-[5]CMP.

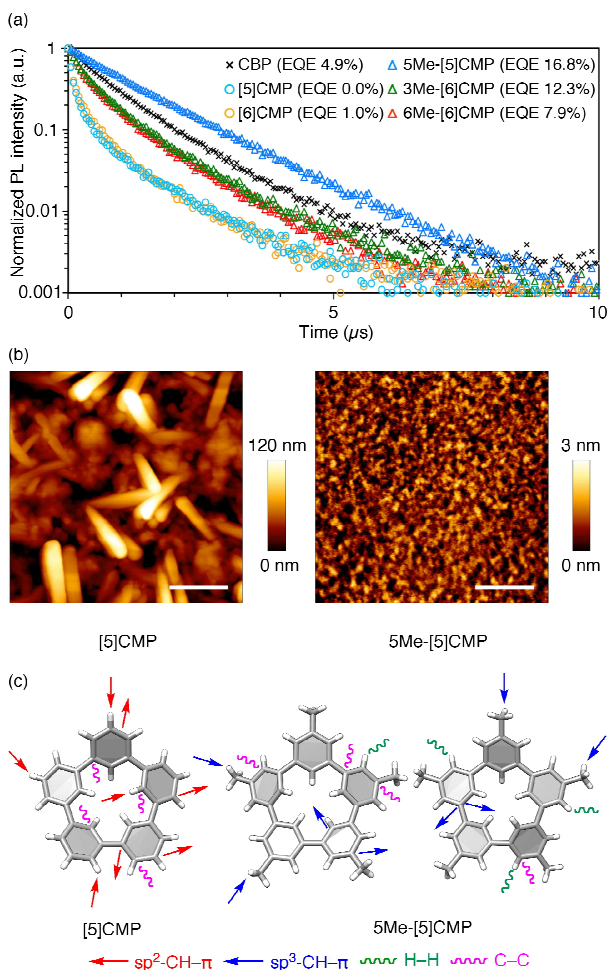


Fig. 4 Fundamental properties of thin films. (a) Photoluminescence decay of $\text{Ir}(\text{ppy})_3$ (6 wt%) at 520 nm in a 40-nm thin film of the host materials with excitation at 335 nm. An identical layer was embedded as the EML in a four-layer OLED to yield the EQE values shown in the graph. See Fig. 2 and Table 1 for the details of device performance. (b) AFM images of thin films of [5]CMP (left) and 5Me-[5]CMP (right) deposited on a glass surface. The horizontal scale bars are 500 nm. (c) Molecular structures and intermolecular contacts of [5]CMP and 5Me-[5]CMP from X-ray diffraction analysis of single crystals. Two crystallographically inequivalent molecules of 5Me-[5]CMP are shown. See ESI for data of other compounds.

Structural information from X-ray diffraction analysis of single crystals

suggested that the differences in the thin film morphologies could be attributed to the differences in the intermolecular contacts. Thus, the sp^2 -CH- π contacts between benzene rings predominated the intermolecular contacts in the [5]CMP crystal, whereas the sp^2 -CH- π contacts were diminished in the 5Me-[5]CMP crystal (Fig. 4c). Instead, in the 5Me-[5]CMP crystal, various intermolecular contacts, such as sp^3 -CH- π , H-H and C-C contacts, appeared, which also resulted in two crystallographically inequivalent molecules in a unit cell. Note that the rotational freedom of the methyl group can also compromise with the various relative orientations of neighboring molecules in the solid.²⁶ We believe that hampering direct benzene-benzene contacts as well as increasing the variety of contacts and conformations preferably contributed to the maintenance of the inherent high E_T value of methylated CMP in the thin film (Table 2).

Single-layer OLED. The single-layer architecture of OLED was then examined with the hydrocarbon macrocycles, m Me-[n]CMP. Despite the preceding studies with multi-component base materials,¹⁰⁻¹² our investigations with m Me-[n]CMP showed that the donor-acceptor design is not a requisite for the highly efficient single-layer OLED. On the other hand, we revealed that a wide bandgap motif of aromatic hydrocarbons is ideal for the multirole, single-component base material and found a requisite property to realize a highly efficient single-layer OLED. We first fabricated a single-layer OLED with CBP as a reference. The single-layer OLED of CBP with 6 wt% of Ir(ppy)₃ (Fig. 1a) emitted electroluminescence with an EQE value of 4.9% (DV = 3.3 V; Fig. 5 and Table 3). The EQE values of 5.3% (DV = 4.8 V) for 6Me-[6]CMP and 7.3% (DV = 4.5

V) for 3Me-[6]CMP with the single-layer architecture containing the doped Ir(ppy)₃ emitter were close to the level of CBP but, hence, not surprising (Fig. 5 and Table 3). However, the EQE value of 22.8% (DV = 5.7 V) recorded with 5Me-[5]CMP was unexpected. The EQE value was even close to the highest, utmost value of preceding OLEDs with the Ir emitters (20–30%) embedded in the materials with donor-acceptor diode designs.⁴⁻¹⁰ To the best of our knowledge, among the multi-component base materials, there exists only one example of single-layer OLED achieving the utmost electro-optical conversion (EQE = 26.8%)¹⁰ which is comparable to the level of the state-of-the-art multi-layer OLEDs.^{4-9,27} An estimate of the light out-coupling efficiency of 20–30%^{6,7,28} indicated that nearly quantitative electro-optical conversion with internal quantum efficiency in the range of 100–76% was achieved in the single-layer OLED with the aromatic hydrocarbon material, 5Me-[5]CMP.

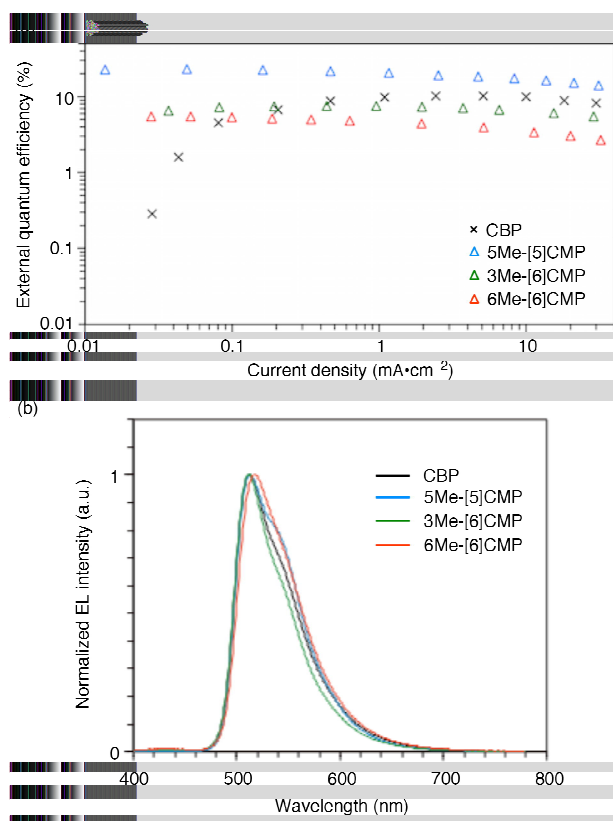


Fig. 5 Performance of single-layer OLED. (a) External quantum efficiency of single-layer OLED plotted against the current density. See Fig. 1a for the device architecture. (b) Electroluminescence spectra at a current density of 0.1 mA·cm⁻².

Table 3 Representative performance data of single-layer phosphorescent OLED^a

base material	EQE (%)	CE (cd·A ⁻¹)	PE (lm·W ⁻¹)	DV (V)
CBP	4.9	9.5	14.0	3.3
5Me-[5]CMP	22.8	94.1	43.5	5.7
3Me-[6]CMP	7.3	30.1	17.3	4.5
6Me-[6]CMP	5.3	21.7	11.4	4.8

^a Performances were evaluated at 0.1 mA·cm⁻², and the Lambertian factors for data calibrations were as follows. For EQE: CBP = 1.80, 5Me-[5]CMP = 0.87, 3Me-[6]CMP = 0.81, 6Me-[6]CMP = 0.87. For PE: CBP = 1.56, 5Me-[5]CMP = 0.84, 3Me-[6]CMP = 0.81, 6Me-[6]CMP = 0.90.

Although we do not fully understand the requisite for the multirole hydrocarbons in the single-layer OLED at this stage, we observed one important and anomalous characteristic of 5Me-[5]CMP in comparison with other *m*Me-[*n*]CMP. The fundamental energetics in the devices were commonly shared among CMP as well as CBP (Fig. 6). However, one peculiar behavior of 5Me-[5]CMP was observed in the *J-V* characteristics of hole-only and electron-only devices (HODs and EODs; Fig. 7).^{11,12} Thus, the driving voltage for 100 mA•cm⁻² of hole current density in the HOD was particularly increased by 18.1 V (from 9.4 V to 27.5 V) upon doping the layer of 5Me-[5]CMP with 6 wt% of Ir(ppy)₃, whereas the increases in the layer of other materials, *i.e.*, 3Me- and 6Me-[6]CMP, were much smaller (<6 V, Fig. 7). An increase of the driving voltage in the EOD for 100-mA•cm⁻² electron current densities was negligible for all the materials (<4 V). When the *J-V* characteristics were interpreted in terms of the charge carrier mobilities through the application of Child's law at the same current density,^{11,12} we observed that the doping of Ir(ppy)₃ resulted in marked and peculiar retardation of the hole mobility in the 5Me-[5]CMP layer (2.2×10^{-5} vs. 9.3×10^{-7} cm²•V⁻¹•s⁻¹; Table 4). We believe that this hole retarding effect of the dopant in the 5Me-[5]CMP layer preferably operated to confine the charge recombination site around the doped region and functioned similarly to the HBL. Preceding studies on Ir(ppy)₃ revealed that the emitter can act as a hole trap at the charge recombination step,^{12,29} and the effective transfer of the hole to the emitter, which was observed particularly with 5Me-[5]CMP in our case, should be favorable for the highly efficient

electroluminescence. This result shows that, in addition to high E_T values,²⁰ a subtle control over the charge mobilities is a requisite for molecular design for the single-layer OLED.

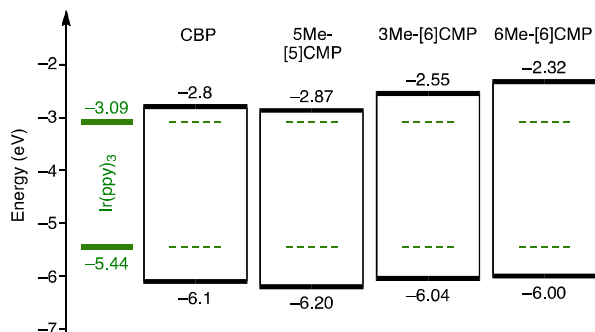


Fig. 6 Energetics of single-layer OLED. All the base materials possessed similar energetics especially in the HOMO levels. The HOMO levels were directly measured by photo-electron spectroscopy in air (PESA), and the LUMO levels were estimated using the optical energy gaps obtained from absorbance onsets of thin films. The data for CBP were acquired from a literature.⁸

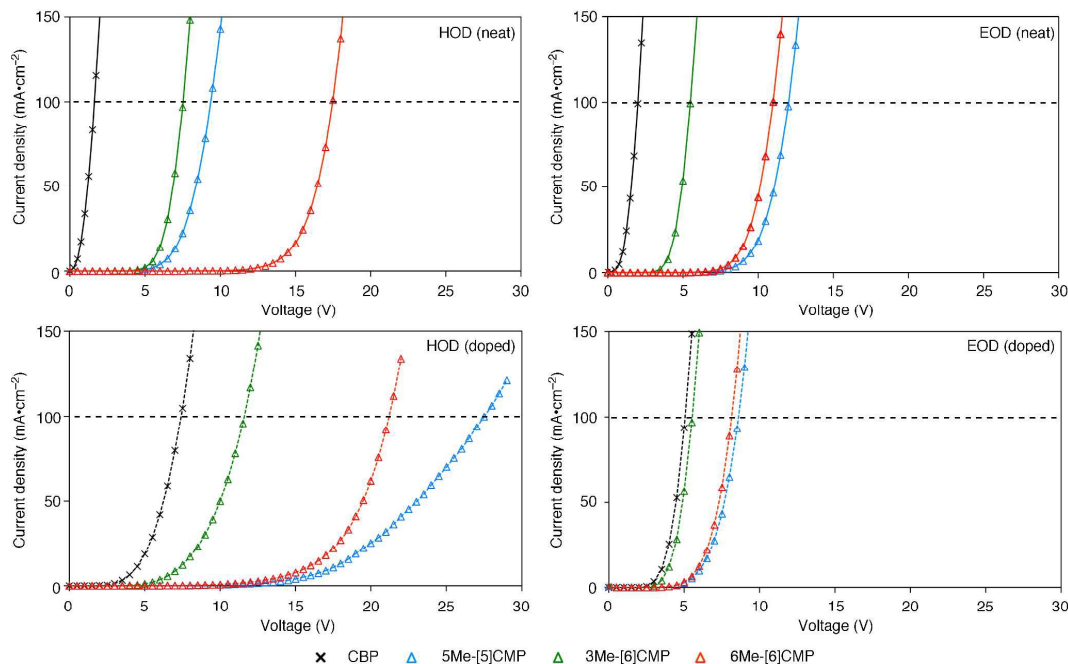


Fig. 7 J - V characteristics of HOD and EOD are shown for the devices in the absence (neat) or presence (doped) of $\text{Ir}(\text{ppy})_3$ (6 wt%). The horizontal broken line shows $100 \text{ mA}\cdot\text{cm}^{-2}$. The HOD device was assembled with an ITO (110 nm)/PEDOT:PSS (30 nm)/organic layer (60 nm)/ α -NPD (20 nm)/Al (100 nm) architecture, and the EOD device was assembled with an ITO (110 nm)/PEDOT:PSS (30 nm)/Ca (5 nm)/organic layer (60 nm)/Cs (1.5 nm)/Al (100 nm) architecture. The organic layer was composed either of a single material (neat) or a material containing 6 wt% $\text{Ir}(\text{ppy})_3$ dopant (doped).

Table 4 Mobility data of HOD and EOD ^a

base material	μ ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) (neat)		μ ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) (doped)	
	hole	electron	hole	electron
CBP	2.1×10^{-4}	1.9×10^{-4}	2.3×10^{-5}	6.8×10^{-5}
5Me-[5]CMP	2.2×10^{-5}	2.0×10^{-5}	9.3×10^{-7}	2.5×10^{-5}
3Me-[6]CMP	4.4×10^{-5}	6.0×10^{-5}	1.2×10^{-5}	6.7×10^{-5}
6Me-[6]CMP	1.1×10^{-5}	2.4×10^{-5}	6.7×10^{-6}	3.2×10^{-5}

^a The mobilities were estimated at $100 \text{ mA}\cdot\text{cm}^{-2}$ from J - V^2 characteristics using Child's law ($J = 9\epsilon\mu V^2/8L^3$) for neat layers and doped layers.

The key structural feature of hydrocarbon base materials was thus deduced as follows: 1. unbiased hydrocarbon motifs for the bipolar charge transport, 2. macrocyclic structures for the high thermal robustness, 3. transparency in the visible light region (*vide infra*), 4. steric design of the periphery to hamper the direct π - π contacts for the high- E_T base materials and 5. steric design of the macrocyclic core for the induction of the hole retarding effect with the emitter. To deduce the origin of the last feature of the hole retarding effect more clearly, we compare 5Me-[5]CMP and *m*Me-[6]CMPs in details. These molecules substantially share similar characteristics and structural features: they have the bipolar transport activities, high thermal robustness, high- E_T values and preferable energetics in the device (Table 2 and Fig. 6) and, consequently, perform comparably as the host in the multi-layer architecture (*vide supra*). We thus concluded that the last requisite of the retarding effect should have a structural origin and, after examining several structural features, we noted conformational flexibilities of the macrocyclic cores as the most probable candidate. As shown in Fig. 8, the energy barriers examined for a dihedral angle at the single-bond linkages were different between 5Me-[5]CMP and 6Me-[6]CMP.³⁰ The energy barrier for one phenylene panel to pass through the macrocyclic pore (dihedral angle = 0°) was 0.6 kcal/mol for 5Me-[5]CMP and 3.8 kcal/mol for 6Me-[6]CMP. In addition, this phenylene rotation for 5Me-[5]CMP accompanied larger structural deviations than that of 6Me-[6]CMP. We thus can expect that 5Me-[5]CMP flexibly adopts various conformations and, upon doing the emitter, increases the intermolecular contacts to accommodate the emitter preferably.

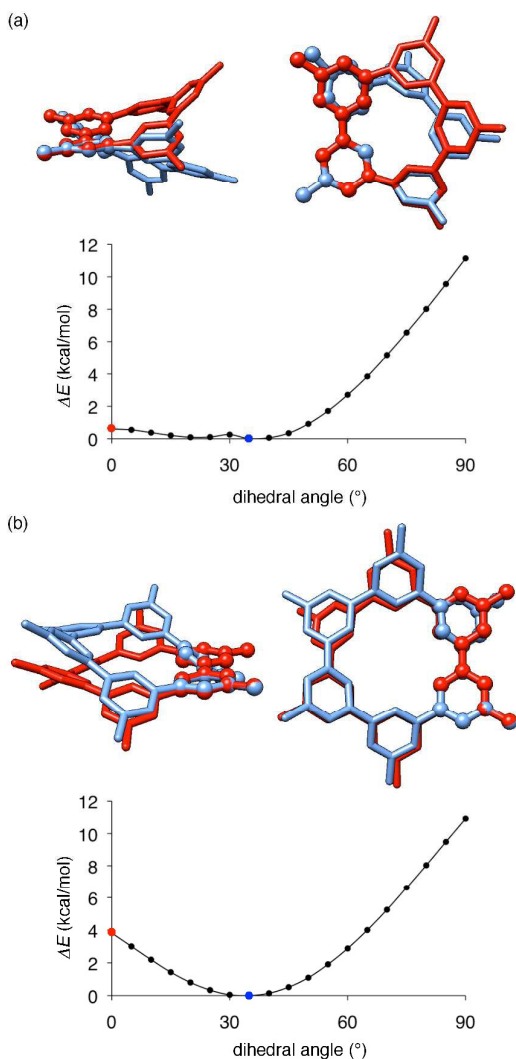


Fig. 8 Structures and energetics for rotation of one phenylene panel. A dihedral angle at the phenylene-phenylene linkages shown with ball-and-stick models was constrained and rotated by 5°. At each constrained point, the most stable structure was obtained by low-mode conformational search calculations (1000 steps) with the MM3* force field (MacroModel), and the energy was obtained by single-point DFT calculations with B3LYP/6-31G(d,p) (Gaussian). The global minima at 35° are shown in blue, and the high energy conformer at 0° are shown in red. The structures were overlaid by minimizing root-mean-square deviation of atomic positions (RMSD) of one reference phenylene panel. (a) 5Me-[5]CMP. RMSD for the all the atoms was 1.633 Å. (b) 6Me-[6]CMP. RMSD for the all the atoms was 0.859 Å.

We finally examined the scope of the single-layer architecture for multiple phosphorescent emitters. Note that aromatic hydrocarbon macrocycles possess an ideally wide window for optoelectronic applications with absorption edges appearing at relatively shorter wavelength for conjugated π -systems, which is another key feature of conjugated macrocycles. As a result of the wide gap between HOMO and LUMO (Fig. S2 and Table S1),^{17,18} absorption edges of CMP were observed around 300 nm (Fig. S3). The absorption is, for instance, much shorter than 350-400 nm of CBP derivatives. We then assembled a white-light-emitting single-layer OLED^{31,32} using a blend of three different phosphorescent emitters, *i.e.*, *fac*-Ir(mpim)₃ for blue,³³ Ir(ppy)₃ for green⁵ and Ir(piq)₃ for red,³⁴ albeit preliminary with an identical architecture as the green device. The device emitted a white light with Commission Internationale de l'Eclairage (CIE) coordinates of (0.30, 0.44) and an EQE value of 10.4% (Fig. 9). The results demonstrated the feasibility of full-color tunings in single-layer OLEDs with aromatic hydrocarbons.

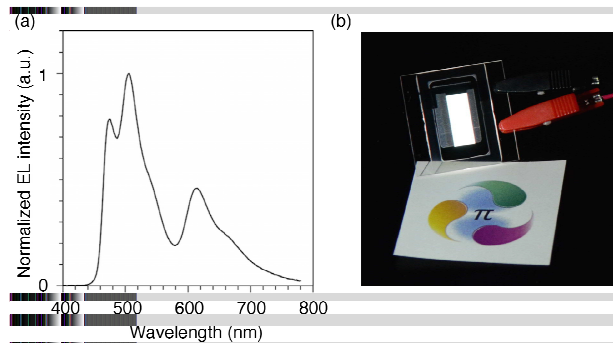


Fig. 9 White OLED with a single-layer architecture. (a) An electroluminescence spectrum at a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$. (b) A picture of the device with an

emitting area of 16.6 mm × 6 mm. The sheet under the device is showing a color reference printed on a white paper, and the original colors can be found at <http://www.jst.go.jp/erato/isobe/>.

Conclusion

We demonstrated that a single, very simple hydrocarbon motif of toluene can be utilized, upon macrocyclization, as the multirole base material of single-layer OLED. The electro-optical conversion in the simplified device reaches the utmost level comparable to the state-of-the-art multi-layer OLEDs, which shows the benefit of the wide bandgap hydrocarbon motifs for the design of the multirole base materials. The overall fabrication processes of the OLEDs were thus substantially simplified from the synthetic stage at the bottom through the one-pot macrocyclization strategy. The molecular design using macrocyclization needs to be supplemented by the steric design to cover all the elemental roles such as bipolar charge carrier transport and high E_T values, and this new guiding principle should be fully explored and developed in the future. The structural chemistry of aromatic hydrocarbon macrocycles is currently being enriched by structural variants and may further stimulate the exploration.³⁵⁻³⁷ A peculiar hole retarding effect of the phosphorescent emitter was observed only in the most successful layer of 5Me-[5]CMP, which implied the importance of conformational flexibility for the preferable accommodation of the emitter. The preceding examples of spiro-structured aromatic hydrocarbons for the host materials may, albeit unintentionally, have utilized similar molecular recognitions with the emitter at their concave sites.³⁸ The versatility of the multirole hydrocarbon materials should also be exploited for other

efficient emitters and may be examined, for instance, with those using thermally assisted delayed fluorescence in the future.²⁸ The future investigations should involve a subtle electronic tuning with the periphery moieties for further improvements of device performances such as the driving voltage.

Experimental section

Theoretical calculations at the solid state. DFT calculations were performed within the generalized-gradient approximation using quantum-ESPRESSO code.³⁹ We employed the exchange-correlation potential with the Perdew-Burke-Ernzerhof parameterization.⁴⁰ Ultrasoft pseudopotentials⁴¹ plain-wave basis sets with cutoff energies of 30 Ry for wave functions and 150 Ry for charge densities and a $1\times 1\times 1$ k-point mesh were used.

Synthesis. Fully methylated macrocycles, n Me-[n]CMP, were synthesized from 3,5-dibromotoluene (10.2 g, 40.8 mmol) by a Ni-mediated macrocyclization reaction.¹⁸ The yields were 15% ($n = 5$; 567 mg, 1.26 mmol), 24% ($n = 6$; 1.05 g, 1.61 mmol), 10% ($n = 7$; 362 mg, 0.570 mmol), 5% ($n = 8$; 205 mg, 0.239 mmol) and 3% ($n = 9$; 100 mg, 0.123 mmol). A partially methylated macrocycle, 3Me-[6]CMP, was synthesized as follows. A mixture of 3,5-dibromotoluene (2.50 g, 10.0 mmol), 1,3-benzenediboronic acid bis(pinacol) ester (3.30 g, 10.0 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (512 mg, 0.495 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (801 mg, 1.95 mmol) and cesium carbonate (16.3 g, 50.0 mmol) in degassed, dry DMF (1.0 L) was stirred at 110 °C for

24 h in a glovebox under nitrogen atmosphere. The reaction mixture was brought outside the glovebox, and water (700 mL) was added. The resulting precipitates were collected by filtration, washed with methanol (10 mL) and dried under vacuum. The solid was extracted with chloroform (200 mL), and the solution was dried on magnesium sulfate and concentrated under vacuum. The crude material was purified by silica gel column chromatography with the eluent of chloroform, by GPC and by washing with 50% methanol/chloroform (7 mL) to afford 3Me-[6]CMP as a white powder in 9% yield (150 mg, 0.300 mmol).

Device. Phosphorescent organic light-emitting diode devices were prepared and evaluated as we reported previously.¹⁸

X-ray analysis. Single crystals for *n*Me-[*n*]CMP (*n* = 5-9) and 3Me-[6]CMP were obtained as described in the synthesis methods and analyzed by X-ray diffraction. The single crystal was mounted on a thin polymer tip with cryoprotectant oil and frozen at the measurement temperature with flash-cooling. The diffraction data were collected and processed with the Rigaku CrystalClear software⁴² or the HKL2000 software program.⁴³ The structure was solved by direct methods using a charge flipping method⁴⁴ or SHELXS⁴⁵ and refined by full-matrix least-squares on F^2 using the SHELX program suite⁴⁴ running on the Rigaku CrystalStructure software program⁴⁶ or the Yadokari-XG 2009 software program.⁴⁷ Geometrical restraints on the disordering solvent molecules, *i.e.*, DFIX, DANG, SIMU and ISOR, were used in the refinements. The non-hydrogen atoms were analyzed anisotropically, and the hydrogen atoms were input at calculated positions and refined with a riding model.

Theoretical calculations on the conformational flexibility. The conformational flexibility of CMPs was analyzed by a protocol that we used for the analysis of cyclophanes.³⁰ Thus, a dihedral angle at the phenylene-phenylene linkages was constrained and rotated by 5°. At each constrained point, the most stable structure was obtained by low-mode conformational search calculations (1000 steps) with the MM3* force field (MacroModel, Maestro v9.8),⁴⁸ and the energy was obtained by single-point DFT calculations with B3LYP/6-31G(d,p) (Gaussian09).⁴⁹

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