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High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules

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We have designed and synthesized a high-efficiency purely organic luminescent material, 2,4-bis{3-(9H-carbazol-9-yl)-9H-carbazol-9-yl}-6-phenyl-1,3,5-triazine (CC2TA) comprising the bicarbazole donor and phenyltriazine acceptor units, which is capable of emitting thermally activated delayed fluorescence. The molecular design of CC2TA allows spatial separation of HOMO and LUMO on the donor and acceptor fragments, respectively, leading to an exceptionally small singlet–triplet exchange energy ($\Delta E_{ST} = 0.06$ eV) together with a high triplet energy. Furthermore, a high external electroluminescence quantum efficiency as high as $11\% \pm 1\%$ has been achieved in the sky-blue organic light-emitting diodes employing CC2TA as an emitter. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4749285]

High-efficiency organic light-emitting diodes (OLEDs) are being developed intensively for next-generation flat-panel displays and general lighting applications[1] owing to their advantages of wide view angles, light weight, flexibility, as well as improved brightness. In the past decade, nearly 100% internal electroluminescence (EL) quantum efficiency (η_{int}) has been achieved by employing transition metal-centered phosphorescent emitters such as iridium(III) and platinum(II) organometallic complexes that can harvest both singlet and triplet excitons by fast intersystem crossing (ISC) for phosphorescence emission.[2–4] However, the efficiency and stability of blue phosphorescence OLEDs are much lower than those reported green and red counterparts. Moreover, a severe efficiency roll-off at high current densities due to triplet–triplet exciton annihilation (TTA) or triplet–polaron annihilation (TPA) is a significant issue of phosphorescence OLEDs.[5]

In contrast, OLEDs incorporating fluorescent emitters provide remarkably high reliability and stability, while their η_{int} should be theoretically limited to ~25% because of the spin statistical limit of 1:3 for the singlet-to-triplet exciton ratio under electrical excitation. Hence, it still remains a challenge to develop efficient luminescent materials rendering high singlet exciton generation efficiency in fluorescence OLEDs. Unlike the case of phosphorescence, one possible way to enhance the fluorescence intensity (i.e., singlet exciton generation efficiency) is up-conversion via TTA.[6] By employing the TTA processes, high external EL quantum efficiencies (η_{ext}) exceeding 10% have been attained in green and red fluorescence OLEDs,[7,8] where the total singlet exciton generation efficiency could be increased up to 62.5%. To maximize the actual efficiency in fluorescence OLEDs, we have recently demonstrated a promising viable mechanism for EL, that is, thermally activated delayed fluorescence (TADF).[9,10] In TADF processes, triplet excitons can be thermally converted into emissive singlet excitons, leading to an increase in the fluorescence intensity. Therefore, it is reasonably anticipated that emitters with a small energy gap (ΔE_{ST}) between the lowest

excited singlet (S_1) and triplet (T_1) states would allow an efficient reverse ISC. In this regard, we previously revealed that a triazine derivative, 2-biphenyl-4,6-bis(1,2-phenylindolo[2,3-*a*]carbazol-11-yl)-1,3,5-triazine (PIC-TRZ) having a rather small ΔE_{ST} (0.11 eV), exhibited an efficient TADF and a high η_{ext} of 5.3% as an emitter in OLEDs.[10] So far, there have been only a few examples of purely organic TADF emitters possessing a small ΔE_{ST} and efficient fluorescence property.[10–12] In this paper, we focus on advanced molecular design of triazine-based TADF luminophors for realizing highly efficient OLEDs. We here demonstrate that the OLEDs based on a designed triazine derivative, 2,4-bis{3-(9H-carbazol-9-yl)-9H-carbazol-9-yl}-6-phenyl-1,3,5-triazine (CC2TA)[13] (Fig. 1(a)), achieve an exceptionally high η_{ext} of $11\% \pm 1\%$ for sky-blue emission.

To understand the electronic and geometrical structure of CC2TA, the quantum chemical calculations have been performed using the TD-DFT/B3LYP/6-31G(d,p) method. As can be seen in Fig. 1(b), the highest occupied molecular orbital (HOMO) of CC2TA is mainly distributed over the outermost carbazolyl units; whereas the lowest unoccupied molecular orbital (LUMO) is localized on the central electron-accepting triazine and its phenyl substituent. Accordingly, CC2TA provides evident spatial separation of HOMO and LUMO distribution, resulting in a notably small calculated ΔE_{ST} of 0.06 eV ($S_1 = 2.91$ eV and $T_1 = 2.85$ eV), which is favorable for a reverse ISC process from its T_1 to S_1 states. If mono-carbazole donor arms, instead of the bicarbazole arms, are attached to the phenyltriazine acceptor core, the HOMO and LUMO are overlapped well on the central triazine ring, resulting in larger ΔE_{ST} of 0.35 eV (see Ref. 13). Thus, in our molecular design, the peripheral bicarbazole donors incorporating Wurster-type[14] (>N–aryl–N<) structures should play a crucial role in achieving such a small ΔE_{ST} of CC2TA, as a consequence of predominant distribution of the HOMO onto the outermost carbazolyl units.

Figure 1(c) depicts the absorption and photoluminescence (PL) spectra of CC2TA measured in different solvents. The lowest-energy absorption peak appears at about 340 nm,

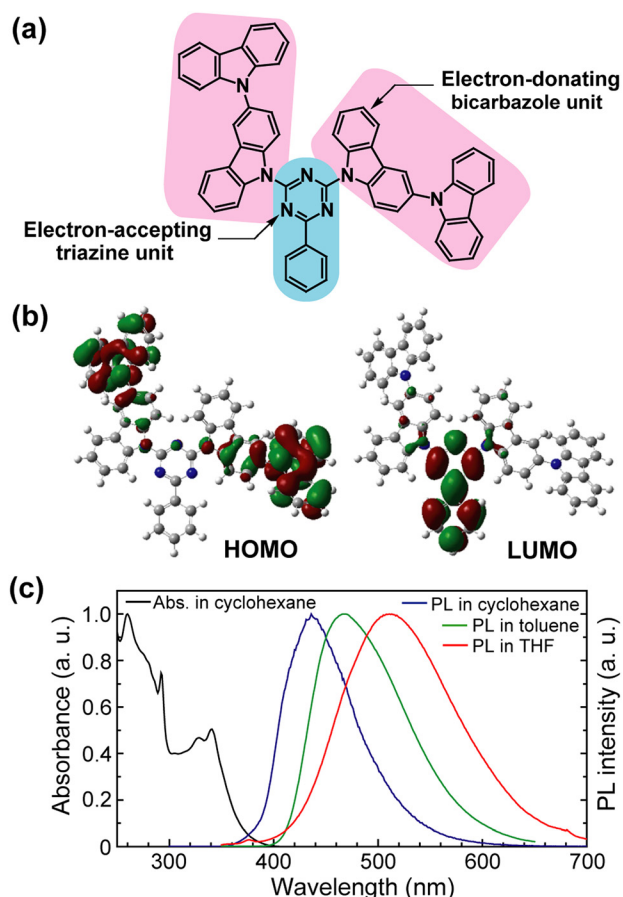[a]Electronic mail: adachi@cstf.kyushu-u.ac.jp.

FIG. 1. (a) Molecular structure and (b) HOMO and LUMO distribution of CC2TA. (c) Room-temperature absorption and PL spectra of CC2TA in different solvents.
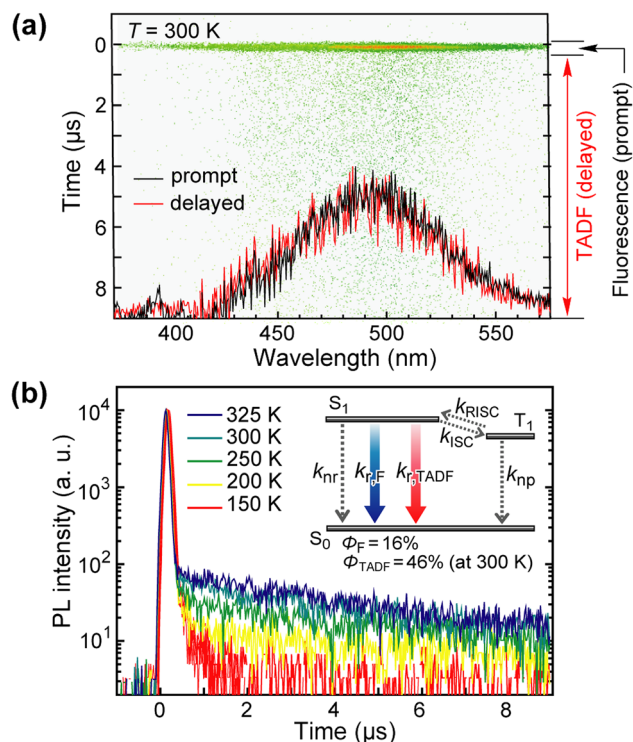

FIG. 2. (a) Streak image and photoluminescence spectra of a 6 wt. % CC2TA:DPEPO film showing the prompt (fluorescence, black) and delayed (TADF, red) components. (b) PL decay profiles for a 6 wt. % CC2TA: DPEPO film measured at 150-325 K. The inset shows energy diagram of CC2TA ($k_{r,F}$: fluorescence decay rate; $k_{r,TADF}$: TADF decay rate; k_{nr}: non-radiative decay rate from S_1 to S_0; k_{ISC}: intersystem crossing rate; k_{RISC}: reverse intersystem crossing rate; k_{np}: non-radiative decay rate from T_1 to S_0; Φ_F: fluorescence efficiency; and Φ_{TADF}: TADF efficiency).

which is almost independent on solvent polarity. In sharp contrast, the PL peak of CC2TA displays obvious red-shifts from 435 nm in non-polar cyclohexane to 513 nm in highly polar tetrahydrofuran (THF) with a gradual decrease of emission intensity. This solvatochromic behavior in PL is attributable to the intramolecular photoinduced charge transfer from the peripheral bicarbazole donor to the central triazine acceptor in CC2TA, leading to a large change in dipole moment in the excited state.

We have analyzed the transient PL characteristics of CC2TA doped into a bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO)[15] host. The triplet energy level of DPEPO ($T_1 = 3.1$ eV) as a host suffices for the prevention of reverse triplet energy transfer from CC2TA. It should be noted that the CC2TA:DPEPO codeposited films with 1, 3, 6, and 10 wt. % doping concentrations give PL quantum efficiencies of 52, 55, 62, and 47%; so that the optimum doping concentration should be close to 6 wt. % in this system. As presented in Fig. 2, a 6 wt. % CC2TA:DPEPO film unambiguously indicates both prompt and delayed fluorescence components, and the PL decay can be fitted by a biexponential model. Because the emission spectra for prompt ($\tau = 27$ ns) and delayed ($\tau = 22$ μs) components are coincident one another, the long tail emissions should be considered to originate in TADF (Fig. 2(a)). The transient PL properties of the CC2TA:DPEPO film have been further studied over a wide range of temperature (Fig. 2(b)). Whilst the delayed component is almost negligible below 150 K, the

quantum efficiency due to delayed fluorescence (Φ_{TADF}) evidently increases with increasing temperature from 150 to 325 K. Thus, the overall PL quantum efficiency reaches to 62%, including 46% of Φ_{TADF}, at room temperature (300 K).

As host materials for CC2TA (TADF emitter), it is desirable that their triplet energy levels are higher than that of CC2TA to prevent reverse energy transfer and to confine triplet excitons on CC2TA molecules. To verify the dependence of the T_1 energy levels of hosts upon TADF efficiencies, thin films of CC2TA in several representative host materials have been fabricated for transient PL measurements. Here, 1,3-bis(carbazol-9-yl)benzene (mCP, $T_1 = 2.90$ eV),[16] 3,5-bis(carbazol-9-yl)pyridine (PYD2, $T_1 = 2.93$ eV),[17] 1,4-bis(triphenylsilyl)benzene (UGH2, $T_1 = 3.5$ eV),[18] as well as DPEPO ($T_1 = 3.1$ eV) have been utilized as a host material for CC2TA (Fig. 3). It is noteworthy that using DPEPO and UGH2 hosts that possess the T_1 higher than 3.1 eV, enhanced TADF quantum efficiencies (Φ_{TADF}) exceeding 45% can be obtained. In contrast, mCP and PYD2 having the T_1 close to CC2TA, give rise to lowering of Φ_{TADF}, which can be attributed to triplet exciton quenching by possible reverse triplet energy transfer from CC2TA to the host molecules.

To demonstrate the practical utility of CC2TA as a TADF emitter, we have fabricated multilayer OLEDs with the following device configuration (Fig. 4(a)): indium-tin-oxide (ITO)/4,4′-bis [N-(1-naphthyl)-N-phenyl]biphenyl diamine (α-NPD, 40 nm) / 6 wt. % CC2TA:mCP (10 nm)/ 6 wt. % CC2TA:DPEPO (20 nm)/DPEPO (10 nm)/1,3,
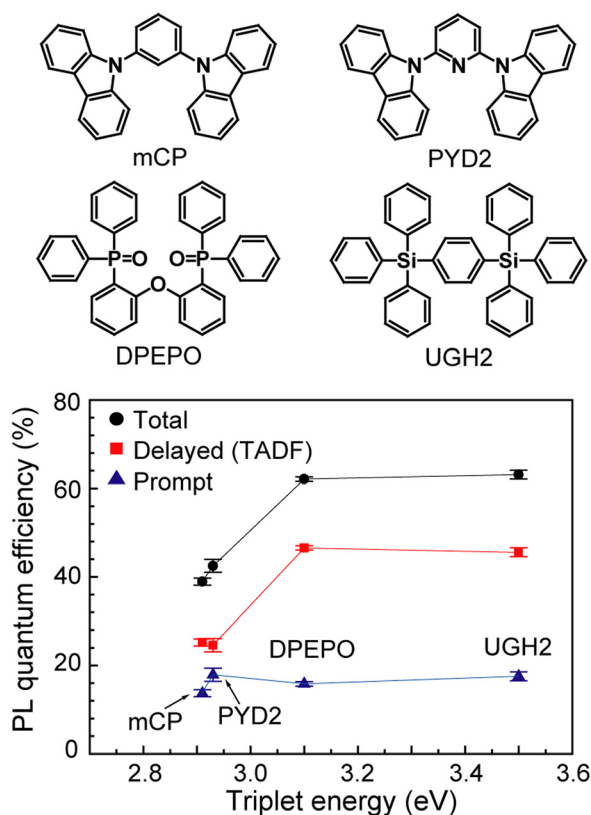
FIG. 3. Molecular structures of host materials tested (top). Relationship between T_1 of host materials and PL quantum efficiencies of 6 wt. % CC2TA:host films.
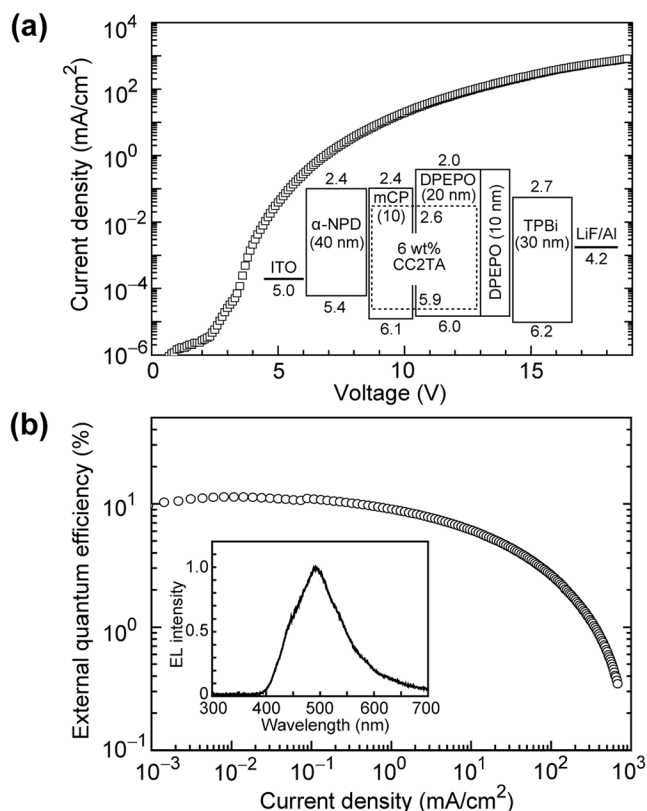

FIG. 4. (a) Current density–voltage (J–V) characteristics and energy-level diagram of the device incorporating CC2TA; (b) external EL quantum efficiency (η_{ext}) as a function of current density (inset: EL spectrum operated at 10 mA/cm^2).

5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi, 30 nm)/ LiF (0.8 nm)/Al (80 nm). In this device, α-NPD and TPBi serve as a hole-transporting layer and an electron-transporting layer, respectively, and LiF is used as an electron-injecting material. It is noted that we adopt a double-emission layer[19] dispersing the CC2TA emitter into both mCP and DPEPO layers having opposite transport properties in order to enlarge the carrier recombination zone.[20] Moreover, a thin layer of DPEPO with a high T_1 as an exciton blocking layer is inserted at the emitter/TPBi interface.

Figure 4 presents the current density–voltage (J–V) and η_{ext} characteristics of the OLEDs. The driving voltage at 10 mA/cm^2 for the device is 9.2 V. Although efficiency roll-off is observed, the η_{ext} is found to reach the maximum of 11% ± 1% at low current densities, which is more than two times higher than the limit of η_{ext} in conventional fluorescence OLEDs. The EL spectra show sky-blue emission from CC2TA (inset of Fig. 4(b)), without any other emission from the adjacent organic layers, indicative of excellent confinement of excitons within the emitting layer.

Under electrical excitation in OLEDs with TADF processes, the triplet excitons are directly generated by carrier recombination and are then converted into the S_1 state through reverse ISC. On this basis, the theoretical maxima of η_{int} can be given by the following equation:[10]

$$\eta_{int} = \eta_{r,S} \times \Phi_F + \eta_{r,s} \times \Phi_{TADF} + \eta_{r,T} \times \Phi_{TADF}/\Phi_{ISC},$$

where $\eta_{r,S}$ is the singlet-exciton production efficiency (25%), $\eta_{r,T}$ is the triple-exciton production efficiency (75%), Φ_F is

the fluorescence quantum efficiency (16%, see Fig. 2), Φ_{TADF} is the TADF quantum efficiency (46%), and Φ_{ISC} is the ISC efficiency ($\sim$84%). Therefore, η_{int} is estimated to be 56%, and the theoretical maximum of η_{ext} will reach to 11% in this system, by assuming a light out-coupling efficiency of ca. 20%. The experimental η_{ext} of 11% ± 1% obtained for the foregoing device is consistent well with the theoretical value presumably because of the appropriate charge carrier injection and transport balance and triplet exciton confinement by suitable hole- and electron-transporting layers.

In summary, we have developed an efficient TADF material CC2TA incorporating bicarbazole donor and phenyl-triazine acceptor fragments. By employing CC2TA as an emitter, we have achieved high-performance TADF-based OLEDs, exhibiting η_{ext} as high as 11% ± 1%. Using the electron-accepting triazine building block tethered by appropriate electron-donating segments would be a versatile and promising strategy to construct high-performance TADF materials and OLEDs.

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[20]For a single-emission layer device: ITO/α-NPD (40 nm)/mCP (10 nm)/6 wt. % CC2TA:DPEPO (20 nm)/DPEPO (10 nm)/TPBi (30 nm)/LiF (0.8 nm)/ Al (80 nm), the driving voltage of 11.9 V at 10 mA/cm^2 and the maximum η_{ext} of 10% were obtained (see Ref. 13).