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Phosphazene-Based Host Materials for the Use in Blue Phosphorescent Organic Light-Emitting Diodes

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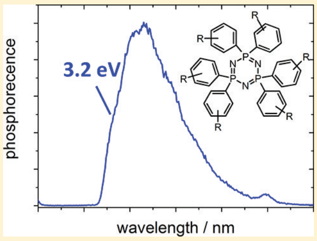

ABSTRACT: We present a series of low-molecular-weight materials based on cyclic phosphazenes for the use as host materials in blue phosphorescent organic light-emitting diodes. Substituted phenyl rings are attached to the central phosphazene ring either via phosphorus−oxygen bonds to yield phenoxy-substituted derivatives or via direct phosphorus−carbon bonds to yield phenyl-substituted derivatives. The phenoxy substituted cyclic phosphazenes were prepared by nucleophilic substitution of the six chlorine atoms in hexachlorocyclotriphosphazene with phenoxy groups, whereas the phenyl substituted cyclic phosphazenes were formed in a cyclocondensation reaction of three equivalents of substituted phosphinic amides. The phenyl substitution leads to materials with superior thermal properties compared to the phenoxy substitution. Because of the nonconjugated linkage to the phosphazene core, the host materials have very high triplet energies of more than 3 eV. In an OLED device using one compound as host for the saturated blue phosphorescent emitter Ir(dbfmi), a peak power efficiency of 7.6 lm W^{-1} and a peak luminance of 5000 cd m^{-2} were achieved.

KEYWORDS: *OLED, blue phosphorescence, ultra high band gap host (UGH), cyclic phosphazenes*

■ INTRODUCTION

Since the first efficient multilayer organic light-emitting diode (OLED) was invented by Tang and van Slyke in 1987, great advances have been made by extensive development of new OLED materials and sophisticated device setups.[1−3] Nowadays, OLEDs are attracting attention because of their capability to realize full color displays and large area lighting with high power efficiency and freedom of design. The key to high efficiencies was the discovery of phosphorescent emitters based on organo-transition metal complexes that are able to harvest both electrogenerated singlet and triplet excitons for light emission. Therefore, the theoretical limit of the internal quantum efficiency reaches 100%.[4] In general, the triplet emitters have to be embedded into a host to avoid concentration quenching.[5] It is essential that the triplet energy of the host is larger compared to the triplet emitter to prevent energy back transfer from the emitter to the host and to confine triplet excitons on the emitter molecules. This restriction becomes particularly challenging when host materials for deep blue phosphors are in the focus of interest, where host triplet energies larger than 3.0 eV are required. Among the commonly used class of carbazole based host materials, some examples like the substituted N-phenylcarbazole 9-(4-tert-butylphenyl)-3,6-ditriphenylsilyl)-carbazole (CzSi, $E(T_1 - S_0)$ = 3.02 eV)[6] and 1,4-bis(4-(carbazol-9-yl)phenyl)cyclohexane (CBPCH, $E(T_1 - S_0)$ = 3.01 eV)[7] show triplet energies close to their intrinsic limit of 3 eV.[8] To provide host materials with even larger triplet band gaps the conjugation of the host molecules must be extremely confined which limits the choice of possible building blocks. Organosilane compounds have been presented as materials with ultra high bandgaps (UGH) and successfully employed in OLEDs as host materials for blue phosphors.[9−12]

Besides organosilane compounds, several phosphorus containing host materials, such as phosphine oxides,[13−15] have been introduced as promising candidates with high triplet energies. Another class of phosphorus containing materials interesting for the use in organic electroluminescent devices are cyclic phosphazenes. The planar nonconjugated 6-membered ring consisting of alternating P- and N-atoms reveals high chemical and thermal stability and exhibits two bonding sites for substituents on each P-atom. Solution-processable dendrimers with various emitters attached to a cyclic phosphazene core have already been reported. Via oxygen−phosphorus bonds emitting fluorescent pyrene units or phosphorescent iridium complexes were attached to the phosphazene core and rigid spherical molecules with high glass transition temperatures were obtained.[16−18] Very recently, the same research group presented phenoxy-carbazole and pyridin-oxy-carbazole functionalized cyclic phosphazene materials and their use as host materials for the greenish-blue triplet emitter FIrpic and the green triplet emitter $Ir(mppy)_3$ in solution processable OLED devices.[19] However, because of their high molecular weight,

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these dendrimers are not suitable for an OLED-fabrication by thermal evaporation.

In this study, we present a series of vacuum processable new phosphazene based host materials for saturated blue phosphorescent emitters. In these materials, substituted phenyl rings were either attached via phosphorus−oxygen bonds (phenoxy substituted cyclic phosphazenes) or via phosphorus−carbon bonds (phenyl substituted cyclic phosphazenes). We present the synthesis of symmetrically substituted organocyclotriphosphazenes together with their thermal and optical properties. The energy levels of the compounds were calculated by density functional theory (DFT). To demonstrate the potential as host material for blue phosphorescent emitters, we have made an OLED device employing an organocyclotriphosphazene host. In Figure 1, the molecular structures of the organocyclotriphosphazenes are depicted.

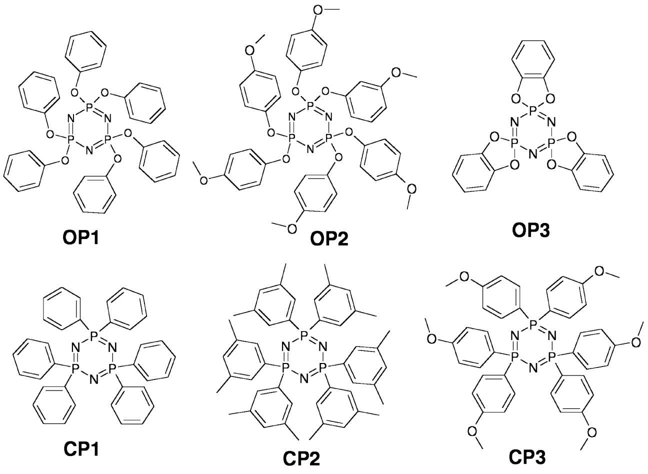


Figure 1. Molecular structures of the cyclic phosphazenes (top) **OP1**−**OP3** with phenoxy substitution and (bottom) **CP1**−**CP3** with phenyl substitution.

■ EXPERIMENTAL SECTION

Materials. All chemicals and reagents were used as received from commercial sources without further purification. All solvents for reactions and purifications were distilled once, except tetrahydrofuran (THF), which was additionally distilled over potassium.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 250 (250 MHz) and $CDCl_3$ as solvent. All data are given as chemical shifts δ (ppm) downfield from $Si(CH_3)_4$. Mass spectra were taken on a Finnigan Mat 8500, Mat 112 S Varian machine using EI-ionization. For optical measurements, 1×10^{-5} M cyclohexane (Uvasol, Merck) solutions of the materials as well as spin coated thin films on quartz substrates were prepared. The UV/vis spectra were measured in solution and on neat films with a Hitachi U-3000 spectrometer. Fluorescence spectra were measured on a Shimadzu spectrofluorophotometer RF-5301PC using excitation at 220 nm. Phosphorescence spectra of thin films have been measured at 5 K (Helium cryostat Optistat CF from Oxford Instruments) applying the technique of time-gated spectroscopy (with fluorescence and phosphorescence lifetime spectrometer FLSP 920 from Edinburgh Instruments). The quantum yield of photoluminescence (η_{PL}) of the 8% Ir(dbfmi)-doped films of **CP1**-**CP3** was measured under N_2 flow using the absolute quantum yield measurement system, model C9920−02 (Hamamatsu), which is based on an integrating sphere, monochromatic excitation at 355 nm and a fibreoptic detector with a multichannel spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA815e machine at a heating rate of 10 K/min in a nitrogen atmosphere. For differential scanning calorimetry measurements (DSC) a Diamond DSC apparatus from Perkin-Elmer was used (heating/cooling rate 10 K/min). The purity of the target compounds was checked with a Waters size exclusion chromatography system (SEC) for oligomers (analytical columns: cross-linked polystyrene gel (Polymer Laboratories), length: 2 × 60 cm, width: 0.8 cm, particle size: 5 μm, pore size 100 Å, eluent THF (0.5 mL/min, 80 bar), polystyrene standard). For the fabrication of OLEDs the organic layers were deposited by thermal evaporation in high vacuum ($<1 \times 10^{-6}$ mbar) onto indium−tin-oxide (ITO, 10 ohm/square) precoated glass substrates. The organic layers and the metal cathode were evaporated without breaking the vacuum.

Computational Methods. The transport levels of the materials used were determined via density functional calculations. For the ionization potential and the electron affinity first the geometry of the neutral as well as the charged states were optimized using the BP86-functional[20,21] in combination with a split-valence basis set (SV(P)) including polarization functions on all heavy atoms.[22] For iridium an effective core potential was employed.[23] For the energetics we performed single point calculations at the optimized geometries using the same functional in combination with a TZVP-basis set.[24] To account for dielectric solid state effects, we used a UPS/IEPS-calibrated version of the conductor like screening model (COSMO)[25] in conjunction with these single-point calculations. All calculations were carried out with the turbomole program package.[26]

Synthetic Procedures. The synthesis of tris[(3-phenyl-1H-benzimidazol-1-yl2(3H)-yliden-1,2-phenylene]-iridium (DPBIC),[35] 2,8-bis(triphenylsilyl)-dibenzofuran (DBFSi),[36] and *mer*-tris(*N*-dibenzofuranyl-*N*′-methylimidazole)iridium(III) (Ir(dbfmi))[27,36] is described in literature.

General Procedure for the Synthesis of Phenoxy-Substituted Phosphazenes. The cyclotriphosphazenes **OP1**−**OP3** were prepared similar to a procedure described in ref 28.

*Hexakisphenoxycyclotriphosphazene (**OP1**).* A suspension of sodium phenolate was prepared by adding sodium hydride (0.55 g, 23 mmol) to phenole (2.16 g, 23 mmol) dissolved in 40 mL of dry THF under argon. Hexachlorocyclotriphosphazene (1.0 g, 2.88 mmol) dissolved in 10 mL of dry THF was added dropwise via syringe and the mixture was stirred under reflux for two days. After removal of the solvent under reduced pressure, the residue was stirred in water for 1 h. The white solid was washed with methanol to remove the excess of phenole. Yield: 1.69 g (85%). EI-MS m/z: 693 ($M^{\bullet+}$, 71), 599 (100), 505 (34). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.21−7.08 (m, 18H), 6.93 (d, 12 H).

*Hexakis(4-methoxyphenoxy)cyclotriphosphazene (**OP2**).* **OP2** was synthesized according to the route described above. The reaction time was 24 h. Yield: 0.62 g (49%). EI-MS m/z: 873 ($M^{\bullet+}$, 100), 749 (78), 626 (8). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 6.83 (m, 12 H), 6.67 (m, 12Hs), 3.79 (s, 18H).

*Tris(phenylenedioxy)cyclotriphosphazene (**OP3**).* Fifteen milliliters of dry THF were added to sodium hydride (1 g, 41.4 mmol) under argon. Catechol (1.9 g, 17.3 mmol) dissolved in 15 mL of dry THF was added dropwise to the NaH solution. After being stirred for 90 min at room temperature, the blue mixture was transferred into a dropping funnel and added dropwise to a solution of hexachlorocyclotriphosphazene (2.0 g, 5.75 mmol) dissolved in 10 mL of dry THF. After stirring at room temperature for 24 h, the same purification procedure as described above was used. Yield: 1.88 g (71%). EI-MS m/z: 459 ($M^{\bullet+}$, 100), 351 (12). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.12−7.00 (m, 24 Hs).

*General Procedure for the Synthesis of Phenyl Substituted Phosphazenes. Bis(3,5-dimethylphenyl)phosphinic Acid (**PAc2**).* 1-Bromo-3,5-dimethylbenzene (13.63 g, 71.44 mmol) was added dropwise to magnesium chips (1.74 g, 71.44 mmol) in absolute THF (80 mL) at room temperature. Once the magnesium was completely dissolved (2 h), a solution of N,N-dimethyl-phosphoryl dichloride $N(Me)_2P(O)Cl_2$ (4.33 mL, 35.72 mmol) in absolute THF (10 mL) was added dropwise by syringe. After 2 h the mixture was poured into an ice-cooled solution of NH_4Cl (30 g) in water (500 mL) for the separation of the formed salt. In a distillation setup with Vigreux column, the THF was distilled off and the residue was treated with conc. HCl (75 mL) at 80 °C. The resulting white solid was dissolved in aqueous NaOH (5.4 g, 300 mL H_2O), and the aqueous layer was twice extracted with ether. The clear aqueous layer was again acidified by the addition of conc. HCl to precipitate the phosphinic acid **PAc2** as white solid. Yield: 6.81 g (70%). EI-MS *m/z*: 274 ($M^{\bullet+}$, 100), 259 (39), 136 (5). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 11.35 (s, 1H, OH), 7.35 (d, 4H), 7.11 (s, 2H), 2.28 (m, 12H, CH_3).

Bis(4-methoxyphenyl)phosphinic Acid (PAc3). The same synthetic procedure as described above was used. Yield: 54% (5.36 g). EI-MS *m/z*: 278 (M•+, 100), 263 (19), 247 (8), 107 (15).^{1}H NMR (250 MHz, CDCl3), δ (ppm): 7.77 (br s, 1H, OH), 7.62 (dd, 4H), 6.83 (dd, 4H), 3.79 (m, 6H).

Bis(3,5-dimethylphenyl)phosphinic Amide. (PAm2). Distilled thionyl chloride (0.87 mL, 12 mmol) was added dropwise to a suspension of bis(3,5-dimethylphenyl)phosphinic acid (1 g, 3.65 mmol) in dry toluene (25 mL) at 55−60 °C and stirred for 20 min. After the removal of the excess of thionyl chloride by distillation ammonia gas was passed into the clear solution for 10 min at 0 °C. In order to separate the NH_4Cl the organic layer was washed with water. Before the extraction with THF the density of the water layer was increased by the addition of sodium chloride. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The phosphinic amide **PAm2** was used for the cyclization reaction without further purification. Yield: 0.98 g (98%). EI-MS *m/z*: 273 ($M^{\bullet+}$, 100), 257 (19).^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.53 (d, 4H), 7.11 (s, 2H), 3.01 (br s, 2H, NH_2), 2.32 (m, 12H).

Bis(3,5-dimethylphenyl)phosphinic Amide (PAm3). The same synthetic pathway as described above was used. Yield: 90% (0.89 g). EI-MS *m/z*: 277(M^+, 100), 170 (45). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.83 (m, 4H), 6.92 (m, 4H), 3.81 (m, 3H), 3.08 (br s, 2 H, NH_2).

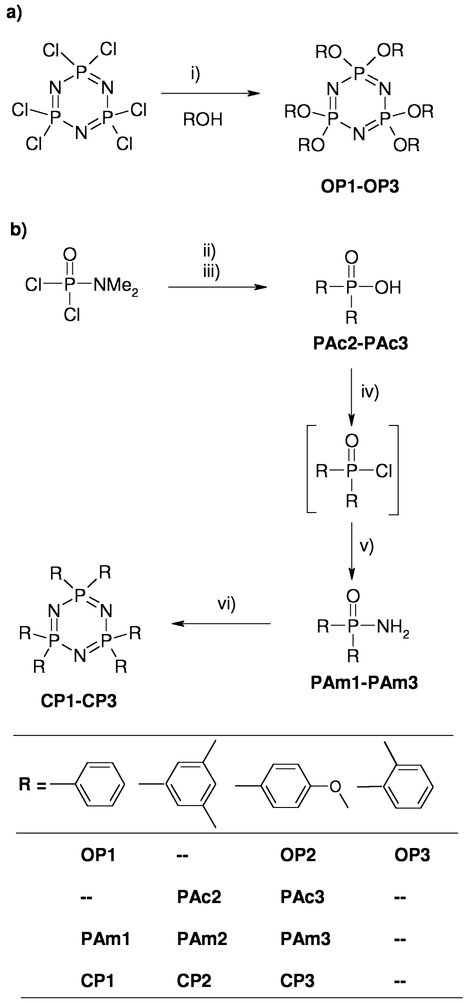
Hexaphenylcyclotriphosphazene (CP1).[29] A suspension of diphenylphosphinic amide (2.0 g, 9.22 mmol), triphenylphosphine (2.9 g, 11.1 mmol), carbon tetrachloride (0.89 mL, 9.22 mmol) and triethylamine (1.3 mL, 9.22 mmol) in dry dichloromethane (25 mL) was refluxed for 5 h. The solvent was removed under reduced pressure. Liquid chromatography on silica gel with hexane:THF mixtures as eluent gave the product as yellowish solid. Yield: 65% (1.2 g). EI-MS *m/z*: 597 ($M^{\bullet+}$, 100), 520 (74), 299 (12), 260 (18), 77 (5). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.76 (m, 12H), 7.30 (m, 18H). ^{13}C NMR ($CDCl_3$), δ (ppm): 138.55 (dt, $C_{\text{P-bound}}$), 130.86 (ps d, C_{meta}), 130.44 (m, C_{para}), 127.98 (ps d, C_{ortho}). Elemental anal. Calcd (%): C, 72.36; H, 5.06; N, 7.03; P, 15.55. Found: C, 72.38; H, 5.08; N, 7.07; P, 15.49.

Hexa-(3,5-dimethylphenyl)-cyclotriphosphazene (CP2). The same procedure for the synthesis as described for **CP1** was applied except the reaction time was extended to 22 h. Yield: 65% (1.2 g). EI-MS *m/z*: 765 ($M^{\bullet+}$, 100), 660 (45), 382 (10), 105 (10).^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.40 (d, 12H), 6.98 (s, 6H), 2.21 (m, 36H). ^{13}C NMR ($CDCl_3$), δ (ppm): 138.35 (dt, $C_{\text{P-bound}}$), 137.16 (ps d, C_{meta}), 131.97 (d, C_{para}), 128.90 (d, C_{ortho}) 21.34 (s, methyl). Elemental anal. Calcd (%): C, 75.27; H, 7.11; N, 5.49; P, 12.13. Found: C, 75.14; H, 7.04; N, 5.54; P, 12.18.

Hexa-(4-methoxyphenyl)-cyclotriphosphazene (CP3). The same procedure for the synthesis as described for **CP1** was applied but the reaction time was extended to 14 h. Yield: 50% (520 mg). EI-MS *m/z*: 777 ($M^{\bullet+}$, 99), 670 (45), 388 (22). ^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.64 (m, 12H), 6.80 (m, 12H), 3.78 (m, 18H). ^{13}C NMR ($CDCl_3$), δ (ppm): 161.24 (m, C_{para}), 132.71 (ps d, C_{meta}), 130.84 (dt, $C_{\text{P-bound}}$), 113.39 (ps d, C_{ortho}), 55.31 (s, methoxy). Elemental anal. Calcd (%): C, 64.86; H, 5.44; N, 5.40; O, 12.34; P, 11.95. Found: C, 65.28; H, 5.44; N, 5.76; O, 12.69; P, 10.81.

■ RESULTS AND DISCUSSION

Synthesis. The phenoxy-substituted phosphazenes **OP1−OP3** have been prepared by nucleophilic substitution of the six chlorine atoms in hexachlorocyclotriphosphazene (Figure 2a). By treatment of the phenols with sodium hydride phenoxylates are formed which replace the chlorine atoms by nucleophilic substitution. The synthesis of the phenyl-substituted derivatives by direct replacement of the six chlorine atoms in hexachlorocyclotriphosphazene is rather difficult. Both an approach by Grignard reaction and by Friedel−Crafts arylation are known to yield mixtures of several substitution products with only small amounts of the hexa-substituted compounds.[30,31] Therefore, we devised the synthetic route to phenyl substituted organocyclotriphosphazenes as sketched in Figure 2b. In a Grignard reaction two chlorine atoms of dichloro-N,N-dimethylphosphinic amide are replaced by the substituted phenyl rings. Acidic workup yields the phenyl substituted phosphinic acids.[32] After treatment with thionyl chloride the intermediately formed phosphinic acid chlorides are directly converted into the substituted phosphinic amides in an amination reaction with gaseous ammonia. The organophosphazenes **CP1−CP3** are formed in a cyclocondensation reaction described by Appel et al.[29] from 3 equiv. of a phenyl substituted phosphinic amide.



OP1	--	OP2	OP3
--	PAc2	PAc3	--
PAm1	PAm2	PAm3	--
CP1	CP2	CP3	--

Figure 2. Synthetic route to (a) phenoxy-substituted cyclic phosphazenes **OP1−OP3** and (b) phenyl-substituted cyclic phosphazenes **CP1−CP3**. Reagents and conditions: (i) NaH, abs. THF, 70 °C, 48 h (catechol: RT, 24 h); (ii) RMgBr, abs. THF, RT, 2 h; (iii) conc. HCl, 80 °C, 1 h; (iv) thionyl chloride, abs. toluene, 55 °C, 20 min; (v) NH_3 (g), 0 °C, 10 min; (vi) PPh_3, CCl_4, NEt_3, benzene, dichloromethane, 40 °C, 5−22 h.

Thermal Analysis. We examined the thermal properties of the organophosphazenes **OP1-OP3** and **CP1-CP3** by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere at a scanning rate of 10 K min^{-1}.

For the application in small molecule OLEDs the materials have to be processable by thermal evaporation. Therefore, the molecular weight of the compounds should not be too high to exclude decomposition during evaporation. As the cyclic phosphazene core bears six substituents it is particularly important to choose confined aromatic units as substituents. In this study, we concentrate on phenyl substituents on the inorganic phosphazene core. All results of the thermal characterization are listed in Table 1.

Table 1. Thermal Properties of OP1-3 and CP1-3[a]

	T_m (°C)	T_{cr} (°C)	T_g (°C)	T_{ID}[b] (°C)
OP1	116	38[c]	−12	260
OP2	107		1	314
OP3	251	173		271
CP1	235	191		285
CP2	214	138	68[d]	280
CP3	281	221	73[d]	337

[a] T_m, melting temperature; T_{cr}, crystallization temperature; T_g, glass transition temperature; and T_{ID}, initial decomposition temperature. [b] T_{ID} is the temperature at which an initial loss of mass was observed in a thermogravimetric experiment with a heating rate of 10 K min^{-1} under nitrogen. [c] Observed only during the heating scan. [d] Observed only during heating scan after quenching from melt.

The phenoxy substituted cyclic phosphazenes **OP1**−**OP3** are thermally stable up to at least 260 °C. However, the high rotational freedom given by the oxygen-linkage leads to very low glass transition temperatures of −12 and 1 °C for compounds **OP1** and **OP2**. Thus, films of **OP1** and **OP2** crystallize readily. In the case of **OP3**, the bifunctional substituents introduce more structural rigidity leading to a much higher melting temperature of 251 °C. Yet, the material does not sublime without decomposition.

We prepared a second series of cyclic phosphazenes with the substituents being attached via direct phosphorus−carbon bonds (**CP1**−**CP3**). All materials show high thermal stability up to at least 280 °C in the TGA measurements and much higher melting temperatures than their phenoxy substituted analogues. **CP1** melts at 235 °C and crystallizes at 191 °C upon cooling. The observed low supercooling of only 44 °C demonstrates the high tendency of **CP1** to crystallize. **CP2** reveals a melting peak at 214 °C and crystallizes upon cooling at 138 °C. Compared to **CP1** the crystallization tendency could be slightly decreased by introducing additional methyl groups as evident from the higher supercooling of 76 °C. **CP3** melts at a temperature of 281 °C and crystallizes at 221 °C upon cooling. Contrary to the twelve methyl groups in **CP2**, the six methoxy groups in **CP3** cause only a slight hindrance of crystallization compared to hexaphenylcyclotriphosphazene **CP1** which is indicated by a supercooling of only 54 °C. In a second DSC experiment the isotropic melts of the samples were quenched with liquid nitrogen before measuring the glass transition temperatures (T_g). The pretreated samples of **CP2** and **CP3** revealed T_g values of 68 and 73 °C, respectively. Although **CP1**−**CP3** show crystalline behavior in the DSC measurements amorphous films can be prepared from solution and evaporation which are morphologically stable over several months at room temperature. To summarize, because of the low glass transition temperatures of **OP1** and **OP2**, no morphologically stable films can be prepared. In contrast, **OP3** reveals higher transition temperatures; however, **OP3** cannot be sublimed without decomposition. Because of their poor thermal properties, the phenoxy substituted cyclic phosphazenes **OP1**−**OP3** are not further considered in this study.

Optical Analysis. For the optical characterization, we measured the UV/vis and photoluminescence spectra of **CP1**−**CP3** in thin films and in cyclohexane solutions (see Figure 3). All materials have an absorption edge in the UV region between 277 and 295 nm. While the absorption of **CP1** and **CP2** are very similar, the absorption of **CP3** is of a different shape and is observed at higher wavelengths. We assign this to the electron donating effect of the methoxy substituents at the para-positions of the phenyl rings. At room temperature, we did not detect any photoluminescence neither in solution nor in film samples. From the wavelength of the absorption edge the optical band gap $\Delta E(S_0 - S_1)$ can be calculated. All cyclic phosphazenes reveal very large band gaps in the range of 4.2 to 4.5 eV. Because the exchange energy of many small molecules is typically in the range of 0.7 to 1 eV,[33] a large triplet energy is expected for **CP1**−**CP3**.

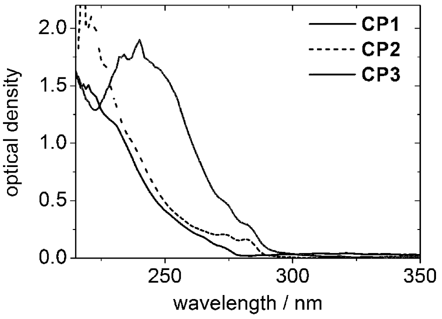


Figure 3. Absorption spectra of thin films of **CP1**−**CP3**.

At low temperatures (5 K), we were able to detect phosphorescence. The phosphorescence spectra are shown in Figure 4. The emission maxima are centered around 395 nm for **CP1** and 410 nm for **CP2** and **CP3**. The highest energy peak is visible as a small shoulder at 363 nm for **CP1** and 382 nm for **CP2** and **CP3** corresponding to very high triplet energies of 3.4 and 3.2 eV, respectively. All results from the photo physical investigations are summarized in Table 2.

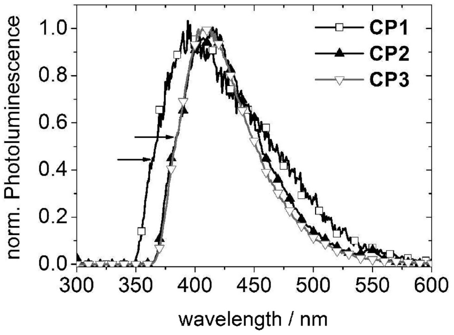


Figure 4. Phosphorescence spectra of **CP1**−**CP3** measured on neat films at 5 K; the arrows indicate the shoulder in the emission spectra taken for the determination of the triplet energy of the compounds.

Table 2. Optical Properties of the Host Materials CP1-CP3

	$\lambda_{EA}{}^{a}$ (nm)	$\Delta E(S_0\text{-}S_1)^{b}$(eV)	$\lambda_{SK}{}^{c}$ (nm)	$\Delta E(T_1\text{-}S_0)$ (eV)	HOMO^{d} (eV)	LUMO^{d} (eV)	$\eta_{PL}{}^{e}$ (%)
CP1	277	4.5	363	3.4	6.47	1.53	71
CP2	288	4.3	382	3.2	5.98	1.35	73
CP3	295	4.2	382	3.2	5.71	1.14	63

[a] Absorption edge measured on neat films at room temperature. [b] The optical band gap was estimated from the onset of the UV/vis absorption of neat films. [c] Wavelength of the highest energy shoulder in the phosphorescence spectra of 100% films at 5 K. [d] Energy levels obtained from DFT-calculations. [e] Quantum yield of photoluminescence measured on film samples of 8% Ir(dbfmi) doped into **CP1−CP3**.

Considering the spatial molecular structure of **CP1** helps to explain the experimental findings. As evident from the geometry optimized molecular structure shown in Figure 5 the pendant phenyl rings are aligned above and below the central plane formed by the P_3N_3 ring. The calculated dihedral angles between the outer phenyl rings and the central ring plane are 48 to 56°. The calculated dihedral angles and bond lengths are consistent with experimental crystallographic data of **CP1**.[34] As no conjugation over the central ring takes place, all phenyl rings are electronically isolated from each other. Thus, in the experiments, the absorption and emission properties of isolated substituted phenyl rings are observed with nearly no influence of the P_3N_3 core.

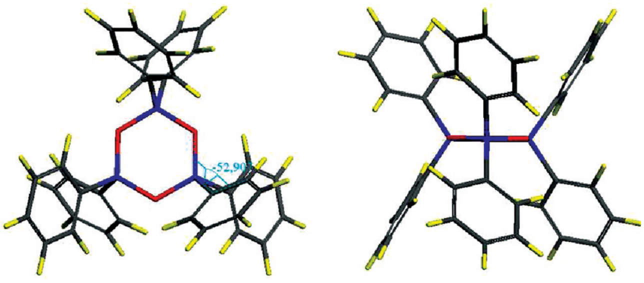


Figure 5. Geometry-optimized molecular structure of CP1.

In Table 2, the energy levels of **CP1-CP3** obtained from DFT-calculations are included. By introducing electron-donating methyl or methoxy groups the HOMO level shifts from 6.47 eV for **CP1** to 5.98 eV (**CP2**) and 5.71 eV (**CP3**), respectively.

To test the ability of the host materials **CP1−CP3** to confine triplet excitons on the emitter molecules we measured the quantum yield of photoluminescence (η_{PL}) on film samples of the saturated blue phosphorescent emitter Ir(dbfmi)[27] ($\Delta E(T_1 - S_0)$ = 2.75 eV, λ_{em}= 450 nm) doped into the host materials **CP1−CP3**. All doped films exhibit high PL quantum yields in the range of 63−73% (cf. Table 2), which demonstrates the ability of **CP1−CP3** to act as efficient host material for the saturated blue emitter Ir(dbfmi).

Single-Carrier Devices. To get a more comprehensive understanding about the charge-carrier transport properties of the novel class of host materials, we prepared single-carrier devices. Because of its high morphological stability, we chose **CP2** for the single-carrier-device tests. Here, the material is sandwiched in varying thicknesses between two chemically doped hole or electron transport layers with high mobilities for holes or electrons. The *J*−*V* characteristics and the device setup are shown in Figure 6.

CP2 is a good hole conductor and a current density of 1 mA cm^{-2} is achieved at 1.6 V for holes. For electrons the current density of 1 mA cm^{-2} is achieved at an even lower voltage of 1 V. The *J*−*V* characteristics show that **CP2** has balanced transport properties for both types of charge carriers.

Phosphorescent Organic Light-Emitting Diodes. While common blue phosphors as for example FIrpic and FIr6 show blue emission tailing to the green region with emission maxima at 472 nm (CIE color coordinates *x* = 0.17, *y* = 0.34)[35] and 458 nm (CIE color coordinates *x* = 0.16, *y* = 0.26),[10] respectively, phosphors with a pure blue emission would be beneficial for solid-state lighting. Because of the high triplet energy of more than 3 eV, the phosphazene-based host materials should be suitable for such saturated blue emitters. Thus, we employed **CP2** in an OLED device as host material

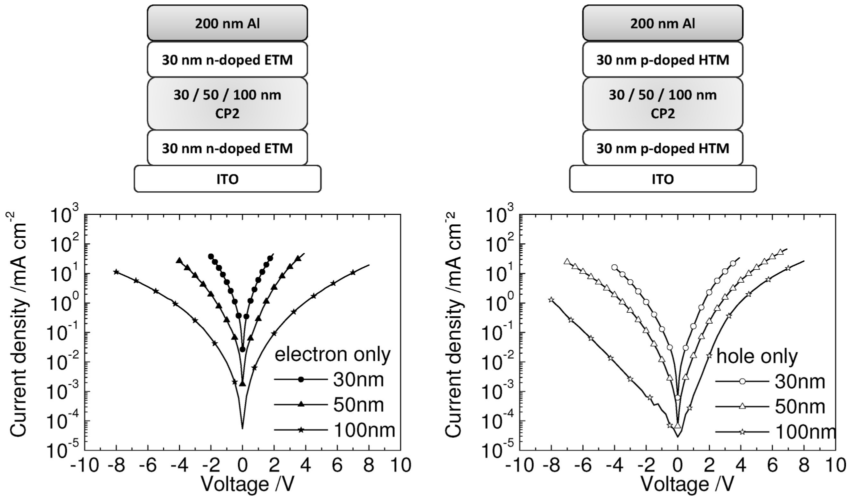


Figure 6. *J*−*V* characteristics of CP2 in e-only device (left) and h-only device (right).

for the pure blue carbene emitter Ir(dbfmi)[27] with a λ_{em} = 450 nm.

The device structure is shown in Figure 7. On top of the indium−tin-oxide (ITO) anode 120 nm of α-NPD p-doped with 10 wt-% molybdenum(VI) oxide were deposited as hole-injection and hole-transporting layer. The additional 10 nm thick hole transporting layer of DPBIC[36] prevents quenching of triplet excitons at the doped NPD-layer. On top a double emission layer of 10 nm of DPBIC doped with 8% Ir(dbfmi) and 40 nm of **CP2** doped with 8% Ir(dbfmi) was deposited. The electron transport within the emission layer takes place over the host **CP2**. The thin emitter doped DPBIC interlayer allows residual electrons to recombine and emit efficiently on the emitter. Ten nanometers of the hole and exciton blocking material 2,8-bis(triphenylsilyl)-dibenzofuran (DBFSi)[37] and 40 nm of the electron-transporting material 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) were deposited. As cathode LiF (0.5 nm)/ Al (100 nm) was used.

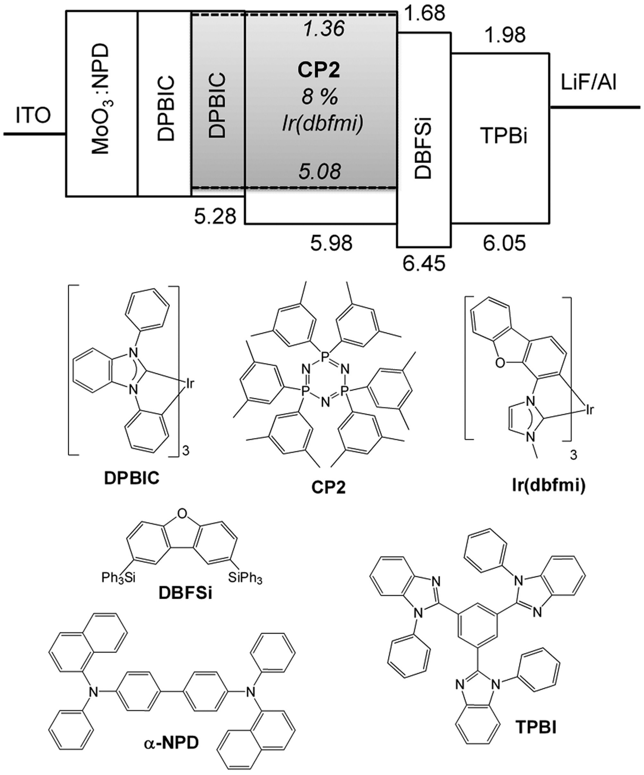


Figure 7. Energy level diagram of the device with **CP2** as host for Ir(dbfmi) and the molecular structures of all materials. Ionization potentials and electron affinity levels of the materials are indicated. The dotted lines represent the levels of the emitter Ir(dbfmi). All HOMO and LUMO levels were taken from density functional theory (DFT) calculations.

Figure 8 (top) shows the current density−voltage−luminance characteristics of the device. A peak luminance of 5000 cd m^{-2} was reached at 13.5 V. The peak power efficiency of 7.6 lm W^{-1} is achieved at 5.5 V. At 100 and 1000 cd m^{-2}, the power efficiencies are 4.9 lm W^{-1} and 2.3 lm W^{-1}, respectively (see Figure 8, bottom). Table 3 lists the device results at different luminances. To the best of our knowledge, this work represents the first report about low-molecular-weight vacuum processable cyclic phosphazene compounds as host materials for an emitter with saturated blue phosphorescence.

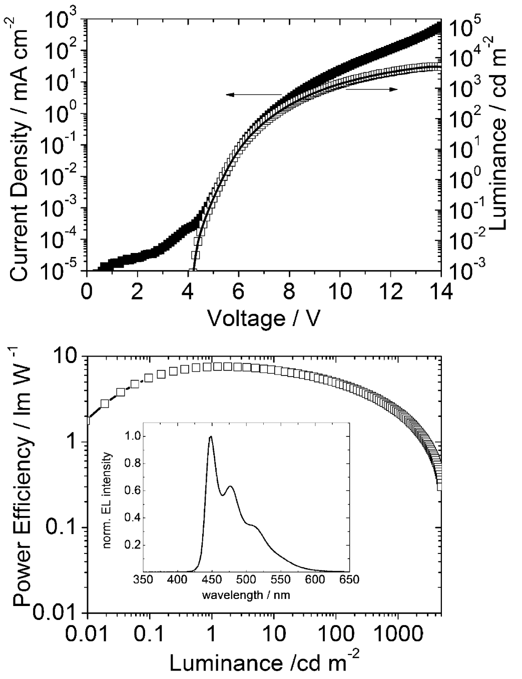


Figure 8. (Top) Current density−voltage characteristics (open squares) and luminance−voltage plot (filled squares). (Bottom) Power efficiency−luminance plot. Inset: EL spectrum of the device.

Table 3. Peak performance data and at 100 cd m^{-2} and 1000 cd m^{-2} using CP2 as host materials for the blue emitter Ir(dbfmi)

turn on voltage (V)	luminous efficiency (cd A^{-1} max, at 100 cd m^{-2}, at 1000 cd m^{-2})	power efficiency (lm W^{-1}) max, at 100 cd m^{-2}, at 1000 cd m^{-2}	CIE *x*, *y*
5.3	13.4, 11.4, 6.7	7.6, 4.9, 2.3	0.15, 0.18

■ CONCLUSION

We have described a novel series of host materials based on cyclic phosphazenes. Substituted phenyl rings were attached to the central phosphazene core either via phosphorus−oxygen bonds (**OP1**−**OP3**) or via phosphorus−carbon bonds (**CP1**−**CP3**). The phenoxy substituted phosphazenes **OP1**-**OP3** revealed high crystallization tendency and poor thermal stability. In contrast, the phenyl substituted phosphazenes **CP1**−**CP3** form morphologically stable films. Because of the nonconjugated linkage via the central phosphazene rings **CP1**-**CP3** exhibit very high triplet energies of more than 3 eV. Thus, energy transfer to even deep blue emitters is possible. The phenyl-substituted phosphazenes reveal balanced transport characteristic for both holes and electrons. In an OLED device, **CP2** was successfully tested as host material for the emitter Ir(dbfmi) with saturated blue emission.

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