Electronic supplementary information

Synthetic progress of organic thermally activated delayed fluorescence emitters via C−H activation and functionalization

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Table S1 List of abbreviations of general terms used in this review

Abbreviations	Full meaning
TADF	**Thermally activated delayed fluorescence**
RISC	**Reverse intersystem crossing**
T_1	**Lowest excited triplet state**
S_1	**Lowest singlet state**
S_0	**Ground state**
k_{RISC}	**Rate of reverse intersystem crossing process**
TTA	**Triplet-triplet annihilation**
D-A	**Donor-acceptor**
ΔE_{ST}	**Energy gap between S_1 and T_1 states**
SOC	**Spin-orbit coupling**
k_r^S	**Radiative rate of S_1 state**
$\langle S\|\hat{H}_{SOC}\|T\rangle$	**SOC matrix element**
k_B	**Boltzmann constant**
T	**Temperature or triplet state**
E_S	**Energy level of S_1 state**
E_T	**Energy level of T_1 state**
E	**Orbital energy**
K	**Electron repulsion energy**
J	**Exchange energy**
HOMO	**Highest occupied molecular orbital**

LUMO	**Lowest unoccupied molecular orbital**
FOMs	**Frontier molecular orbitals**
MR-TADF	**Multiple-resonance thermally activated delayed fluorescence**
FWHM	**Full-width at half-maximum**
MLCT	**Metal-to-ligand charge transfer**
LMCT	**Ligand-to-metal charge transfer**
LLCT	**Ligand-to-ligand charge transfer**
MADF	**Metal-assisted delayed fluorescence**
PF	**Prompt fluorescence**
DF	**Delayed fluorescence**
k_{ISC}	**Rate of intersystem crossing process**
k_r^T	**Radiative rate of T_1 state**
CT	**Charge transfer**
LE	**Locally excited**
Phos	**Phosphorescence**
k_{nr}^S	**Non-radiative rate of S_1 state**
k_{CQ}	**Rate of concentration quenching of T_1 state**
k_{IC}	**Rate of internal conversion**
k_{RIC}	**Rate of reverse internal conversion**
HFC	**Hyperfine coupling**
OLEDs	**Organic light-emitting diodes**
EQE_{max}	**Maximum external quantum efficiency**

ECL	**Electrogenerated chemiluminescence**
PDT	**Photodynamic therapy**
TTA-UC	**Triplet-triplet-annihilation upconversion**
3D	**Three-dimensional**
SN_{Ar}	**Aromatic nucleophilic substitution**
SE_{Ar}	**Aromatic electrophilic substitution**
PLQY	**Photoluminescence quantum yield**
DGs	**Directing groups**
LG	**Leaving group**
M	**Metal**
R. T.	**Room temperature**
AIDF	**Aggregation-induced delayed fluorescence**
$\Theta_{//}$	**Horizontal dipole ratio**
RTP	**Room temperature phosphorescence**
EWG	**Electron-withdrawing group**
MCL	**Mechanochromic luminescence**
CD	**Circular dichroism**
CPL	**Circularly polarized luminescence**
CPEL	**Circularly polarized electroluminescence**
CPPL	**Circularly polarized photoluminescence**
g_{EL}	**Circularly polarized electroluminescent dissymmetry factor**
CP-TADF	**Circularly polarized thermally activated delayed fluorescence**

CP-MR-TADF	**Circularly polarized multiple-resonance thermally activated delayed fluorescence**
EL	**Electroluminescence**
PL	**Photoluminescence**
MCz	**1-Methylcarbazole**
θ_{DA}	**Torsion angle between donor and acceptor**
τ_d	**Lifetime of delayed fluorescence**
TSCT	**Through-space charge transfer**
SRCT	**Short-range charge transfer**
LRCT	**Long-range charge transfer**
DFT	**Density functional theory**
E_{HOMO}	**HOMO energy level**
TSF	**TADF-sensitized fluorescence**
TST	**TADF-sensitized TADF**

Table S2 List of abbreviations of reagents and building blocks used in this review

Abbreviations	Full meaning	Abbreviations	Full meaning
$Pd(OAc)_2$	Palladium(II) acetate	$Pd(PPh_3)_2Cl_2$	Bis(triphenylphosphine)palladium(II) dichloride
AgOAc	Silver(I) acetate	ICz	Indolo[3,2,1-*jk*]carbazole
NBS	*N*-Bromosuccinimide	PAH	Polycyclic aromatic hydrocarbons
PTSA	*p*-Toluenesulfonic acid	MeIAc	12*b*-Methyl-5,12*b*-dihydroindeno[1,2,3-*kl*]acridine
o-DCB	1,2-Dichlorobenzene	DMSO	Dimethyl sulfoxide
$RuCl_3$	Ruthenium(III) chloride	dppf	1,1'-Bis(diphenylphosphino)ferrocene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene	$Pd(dba)_2$	Bis(dibenzylideneacetone)palladium(0)
DME	1,2-Dimethoxyethane	P(*o*-tolyl)$_3$	Tri(o-tolyl)phosphine
K_2CO_3	Potassium(II) carbonate	CsF	Cesium(I) fluoride
MeI	Methyl iodide	CH_3CN	Acetonitrile
$Rh(PPh_3)_3Cl$	Rhodium(I) tris(triphenylphosphine) chloride	CH_2Cl_2	Dichloromethane
MnO_2	Manganese(IV) dioxide	CF_3COOH	Trifluoroacetic acid

$Zn(OAc)_2$	Zinc(II) acetate	$[Ir(COD)OMe]_2$	(1,5-Cyclooctadiene)(methoxy)iridium(I) dimer
PhCl	Chlorobenzene	dtbpy	4,4'-Di-*tert*-butyl-2,2'-bipyridine
$[Ru(p\text{-cymene})Cl_2]_2$	Dichloro(*p*-cymene)ruthenium(II) dimer	$(BPin)_2$	4,4,5,5-Tetramethyl-2-(tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane
PCy_3	Tricyclohexyl phosphine	HBPin	4,4,5,5-Tetramethyl-1,3,2-dioxaborolane
$NaHCO_3$	Sodium(I) bicarbonate	Czp	Carbazolophane, indolo[2.2]paracyclophane
DMF	*N*,*N*-Dimethylformamide	CuCl	Cuprous(I) chloride
TfOH	Trifluoromethanesulfonic acid	KOH	Potassium(I) hydroxide
$AgSbF_6$	Silver(I) hexafluoroantimonate	BICOL	Bicarbazolediol
PivOH	Pivalic acid	$VO(OAc)_2$	Vanadium(IV) acetate
DCE	1,2-Dichloroethane	BDMAc	9,9,9',9'-tetramethyl-9,10-dihydro-9'*H*-2,10'-biacridine
$Pd(acac)_2$	Palladium(II) acetylacetonate	DCM	Dichloromethane
NaOAc	Sodium(I) acetate	bpy	*o*-Phenanthroline
$[Cp^*RhCl_2]_2$	Dichloropentamethylcyclopentadien	[Ru-	Dichlorodi-μ-

	ylrhodium(III) dimer	complex6]$_2$	chlorobis[(1,2,3,6,7,8-*η*-2,7-dimethyl-2,6-octadiene-1,8-diyl]diruthenium(IV)
$Cu(OAc)_2$	Copper(II) acetate	PhCl	Chlorobenzene
$Zn(OTf)_2$	Zinc(II) trifluoromethanesulfonate	CH_3COOH	Acetic acid
AgOTf	Silver(I) trifluoromethanesulfonate	C_2Cl_4	Tetrachloroethene
Ag_2O	Silver(I) oxide	DCz	3,3',6,6'-tetra-tert-butyl-9*H*-1,9'-bicarbazole
Na_2HPO_4	Sodium(I) dihydrogen phosphate	BBr_3	Boron tribromide
HFIP	Hexafluoroisopropanol	DIPEA	Diisopropylethylamine
THF	Tetrahydrofuran	Et_3N	Triethylamine
CuI	Cuprous(I) iodide	PA	*N*^{1},*N*^{1},*N*^{3},*N*^{3},*N*^{5},*N*^{5}-hexaphenylbenzene-1,3,5-triamine
Phen	1,10-Phenanthroline	1,2,4-TCB	1,2,4-Trichlorobenzene
K_3PO_4	Potassium(I) phosphate	BI_3	Boron triiodide
K_2CO_3	Potassium(I) carbonate	BPh_3	Triphenylboron
PPh_3	Triphenylphosphine	dtpy	2,6-Di-*tert*-butylpyridine
Ag_2CO_3	Silver(I) carbonate	$K_2S_2O_8$	Potassium(I) persulfate
^{t}Bu$_3$PHBF$_4$	Tri-*tert*-butylphosphonium tetrafluoroborate	TBAB	Tetrabutylammonium bromide
MCz	1-methyl-9*H*-carbazole	TBHP	*tert*-Butyl hydroperoxide

DMCz	**1,8-dimethyl-9*H*-carbazole**	**^{t}BuPh**	***tert*-Butylbenzene**
TMCz	**1,3,6,8-tetramethyl-9*H*-carbazole**	**I_2**	**Iodine**
Cy_3PHBF_4	**Tricyclohexylphosphine tetrafluoroborate**	**Se**	**Selenium(0)**
Tol	**Toluene**	**SeO_2**	**Selenium(IV) dioxide**
Pd-PCy_3-G3	**Methanesulfonato(tricyclohexylphosphine)(2'-aMino-1,1'-biphenyl-2-yl)palladium(II)**	**LDA**	**Lithium(I) diisopropylamide**
DMA	***N*,*N*-Dimethylacetamide**	**DMPU**	**1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone**
IPr·HCl	**1,3-bis(2,6-di-*i*-propylphenyl) imidazolium chloride**	**TXO**	**Thioxanthone**
$Pd_2(dba)_3$	**Tris(dibenzylideneacetone)dipalladium(0)**	**TsOH·H_2O**	***p*-Toluenesulfonic acid monohydrate**
XPhos	**2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl**	**KI**	**Potassium(I) iodide**
P^{t}Bu_3	**Tri-*tert*-butylphosphine**	**DCP**	**Dicumyl peroxide**
TFE	**2,2,2-trifluoroethanol**	**SpA**	**Spiro-acridan**
$Pd(PCy_3)_2Cl_2$	**Bis(tricyclohexylphosphine)palladium(II) dichloride**		

Table S3 Summary of photophysical properties and device performance of TADF emitters synthesized from directing group-involved C−H bond activation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
*o*PTC	455	47	57.9	0.02	500	19.9	(0.22, 0.40)	[70]
*o*PTBC	561	58	4.6	0.007	540	17.8	(0.35, 0.56)	[72]
*o*AcTBC	509	84	17.4	0.034	512	20.9	(0.23, 0.53)	[73]
*o*SpTBC	497	93	16.9	0.023	508	26.8	(0.21, 0.49)	[73]
DMAC-BPI	510	96	3.3	0.02	508	24.7	(0.24, 0.49)	[77]
DPAC-BPI	472	11	27	0.15	-	-	-	[78]
DPAC-BPI-CN	525	90	3.0	0.07	531	26.2	(0.24, 0.49)	[78]
TMCzSe	488	86	26.7	0.09	494	25.5	(0.21, 0.46)	[80]
PXZ-ICO	564	17	343	0.14	-	-	-	[85]
5a	573	3	7.2	-	-	-	-	[86]
DMAC-2,3-*c*-BTIQO	456	-	11.4	0.12	474	25.4	(0.15, 0.23)	[87]
7a	425	26	14.6				-	[88]
7b	450	10	24.7				-	[88]

(a) The peak wavelength (λ_{PL}) of fluorescent spectra, (b) photoluminescence quantum yields (PLQY), (c) lifetime of delayed fluorescence (τ_d), (d) energy gap (ΔE_{ST}) between singlet (S_1) and triplet (T_1) excited states in solution or film state. (e) The peak wavelength (λ_{EL}) of electroluminescent spectra, (f) maximum external quantum efficiency (EQE_{max}), and (g) Commission Internationale de L'Eclairage (CIE) coordinate of electroluminescence.

Table S4 Summary of photophysical properties and device performance of TADF emitters synthesized from electron-deficient arene C−H bond activation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
$5CzDPhCF_3$	431	27	0.14	0.23	431	2.0	(0.16, 0.07)	[91]
2	507	89	9.8	0.05	512	18.2	(0.25, 0.53)	[93]
CNCN	480	50	1.74	0.017	468	18.3	(0.15, 0.17)	[96]
$CNCF_3$	470	39	0.96	0.025	471	6.6	(0.18, 0.26)	[96]
CNCOA	483	37	2.06	0.015	495	5.6	(0.22, 0.40)	[96]
CNCOAM	472	44	1.76	0.015	457	14.1	(0.15, 0.13)	[96]
2-PXZ-PRB	504	25	58.5	0.34	518	13.6	-	[98]
6-PXZ-PRB	535	38	48.1	0.21	550	15.5	-	[98]
8-PXZ-PRB	522	27	43.4	0.29	530	11.1	-	[98]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S5 Summary of photophysical properties and device performance of carbazole derivatives (from *ortho*-halodiarylamines intramolecular C−H arylation)-based TADF emitters

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
MCz-TRZ	435	51.3	24.8	0.23	450	13.1	(0.15, 0.11)	[100]
MCz-PM	420	42.1	159.9	0.21	458	7.5	(0.17, 0.18)	[100]
MCz-XT	466	86	11.3	0.04	460	24.0	(0.15, 0.15)	[102]
2MCz-XT	483	91	1.0	0.01	482	32.1	(0.17, 0.30)	[102]
CzBP-1M	-	32.3	94	0.12	-	-	-	[103]
CzBP-2M	-	1.2	63	0.11	-	-	-	[103]
TAZ-1	468	88	8.4	0.15	478	17.7	(0.16, 0.25)	[104]
TAZ-2	476	100	6.6	0.10	479	21.2	(0.16, 0.27)	[104]
QBO	455	83	0.65	0.01	460	20.5	(0.14, 0.12)	[105]
QXT	489	96	0.97	0.02	481	24.9	(0.16, 0.30)	[105]
4	443	86	3.49	0.12	-	13.3	(0.14, 0.16)	[106]
Cz-TRZ2	465	98	3.5	0.07	-	22.0	-	[107]
CF_3	450	36	0.19/3.1	0.07	-	-	-	[108]
tmCzAZB	451	56	162.4	0.26	464	12.4	(0.14, 0.15)	[109]
TMCzSe	488	85.9	26.7	0.09	497	25.5	(0.21, 0.46)	[80]
MCz-XT	478	98	1.20	0.011	485	11.1	-	[110]
MCz-BS	476	92	1.9	0.11	478	21.6	(0.14, 0.26)	[111]
TMCz-BO	467	98	0.75	0.020	471	20.7	(0.14, 0.28)	[112]

TMCz-3P	477	76	14.5	0.134	479	20.4	(0.14, 0.26)	[112]
MCz-BSBS	476	100	0.78	0.01	473	20.1	(0.13, 0.20)	[113]
MCz-BOBO	483	93	2.7	0.17	484	25.9	(0.14, 0.33)	[113]
MCz-TXT	490	92	0.75	0.030	497	25.8	(0.21, 0.46)	[114]
MCz-XT	482	95	0.94	0.010	489	25.5	(0.19, 0.42)	[114]
TMCzBCO	520	84	0.99	0.007	532	24.7	(0.33, 0.59)	[115]
TMCz-DMTD	430	57.7	2.6	0.12	448	8.7	(0.16, 0.11)	[116]
1	493	92	6.8	0.02	494	20.9	(0.20, 0.42)	[117]
TMCz-DiKTa	501	76	22	0.08	527	20.2	(0.32, 0.60)	[118]
3TMCz-DiKTa	577	18	3.0	0.01	-	-	-	[118]
TCz-TRZ	457	77	38	0.27	456	10.4	(0.16, 0.14)	[119]
TCz-TRZ(Me)	451	60	51	0.16	448	11.1	(0.17, 0.18)	[119]
TCz-TRZ(Me′)	444	80	58	0.12	450	0.7	(0.20, 0.23)	[119]
TCz-TRZ(Me2p)	442	46	39	0.14	447	0.9	(0.20, 0.21)	[119]
TCz-TRZ(Me2o)	435	47	37	0.18	444	2.8	(0.23, 0.29)	[119]
IDAC-MCO	498	81	22	0.09	516	18.0	(0.28, 0.48)	[120]
IDAC-TRZ	533	90	13	0.02	540	20.5	(0.36, 0.55)	[120]
CNCzpPhTRZ	458	65	135.0	0.23	456	7.4	(0.19, 0.18)	[121]
CF_3CzpPhTRZ	456	70	158.3	0.22	460	11.6	(0.19, 0.20)	[121]
DCzpTRZtBu	455	41	-	0.115	475	3.2	(0.17, 0.26)	[122]
dtBuCzDCzpTRZtBu	455	37	9.7	0.110	478	4.0	(0.19, 0.30)	[122]
dMeOCzDCzpTRZtBu	490	41	7.7	0.070	515	8.2	(0.24, 0.50)	[122]

B^2TPNF_2	527	29	2.17	0.00	-	-	-	[123]
B^2CNPyF_2	488	23	1.84	0.22	-	-	-	[123]
(*R*)-Czp-*t*BuCzB	478	98	41.8	0.09	479	32.1	(0.11, 0.21)	[124]
(*R*)-Czp-POAB	498	96	62.4	0.13	513	28.7	(0.23, 0.65)	[124]
BN-DICz	533	99.4	495.9	0.26	541	31.5	(0.30, 0.58)	[125]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S6 Summary of photophysical properties and device performance of carbazole derivatives (from *ortho*-halogenated phenyl carbazole intramolecular C−H arylation)-based TADF emitters

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	FWHM[h]	Ref.
tBisICz	442	95	12500	0.29	445	15.1	(0.16, 0.05)	22	[143]
tPBisICz	450	91	1740	0.27	452	23.1	(0.15, 0.05)	21	[143]
$DiICzMes_4$	451	82	433	0.26	446	16.5	(0.15, 0.11)	-	[144]
10a	502	17	3.6	0.26	-	-	-		[145]
10b	519	45	3.5	0.15	-	-	-		[145]
10c	505	16	1.6	0.28	-	-	-		[145]
10e	519	37	1.6	0.29	-	-	-		[145]
10f	617	86	1.0	-0.35	-	10	-		[145]
10h	507	37	1.6	0.29	-	12	-		[145]
10i	517	9	1.2	0.12	-	-	-		[145]
10j	500	19	13.0	0.24	-	-	-		[145]
10k	508	19	1.8	0.25	-	-	-		[145]
10l	500	16	1.3	0.27	-	-	-		[145]
10m	503	17	0.79	0.37	-	-	-		[145]
10n	532	30	0.86	0.26	-	-	-		[145]
VTCzBN	496	98	9.9	0.06	499	31.7	(0.14, 0.56)	38	[147]
TCz-VTCzBN	521	98	8.7	< 0.01	524	32.2	(0.22, 0.71)	37	[147]

IPzIDCz	525	76	2.9	0.07	531	23.9	(0.37, 0.57)	-	[148]
ImIDCz	478	51	704	-	-	-	-	-	[148]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, (g) CIE coordinate, and (h) FWHM of electroluminescence.

Table S7 Summary of photophysical properties and device performance of TADF emitters accessed from dehalogenated C−H arylation with forming 5/6-mermbered carbon ring

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
DMAC-SFNP	545	-	88.6	0.27	-	32.2	-	[149]
DMAC-^{t}BuSFNP	540	-	53.7	0.32	-	18.5	-	[149]
DBCP	557	89	30.0	0.10	544	20.2	(0.38, 0.57)	[151]
CNTP-DMAC	~470	58	41	0.34	~480	15.6	(0.18, 0.30)	[153]
TRZ-MeIAc	473	89	82.3	0.19	494	20.3	(0.18, 0.38)	[155]
NID-MeIAc	565	86	235.4	0.22	589	23.7	(0.53, 0.47)	[155]
BN-MeIAc	497	96	28.1	0.11	504	37.2	(0.12, 0.63)	[157]
37 + π	529	74	1.1/3.3		-	-	-	[158]
38 + π	519	49	0.41/1.7		-	-	-	[158]
IT-TRZ	505	98	2.2	0.03	-	35.8	-	[159]
2S-TRZ	507	99	2.4	0.03	-	32.6	-	[159]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S8 Summary of photophysical properties and device performance of TADF emitters from Ir-catalyzed C−H borylation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	FWHM[h] (nm)	Ref.
Phox-$^{Me}\pi$	568	65	1.3	0.04	-	-	-	-	[169]
Phox-$^{MeO}\pi$	598	40	1.6	0.03	-	-	-	-	[169]
^{MeO3}Ph-$^{FMe}\pi$	477	85	5.5	0.03	-	-	-	-	[169]
poly(DMTPA-DCB)	512	64	0.7	0.22	-	-	-	-	[171]
poly(TMTPA-DCB)	532	96	2.3	0.09	-	24.0	(0.34, 0.57)	-	[171]
CNQxP-BDT-TIPS	-	-	1860	0.18	-	-	-	-	[173]
DTPz-BDT-TIPS	-	1	26000	0.40	-	-	-	-	[174]
DtCzB-DPTRZ	507	94	787.5	0.18	532	24.6	(0.33, 0.63)	39	[176]
DtCzB-TPTRZ	477	97	83.5	0.11	516	29.8	(0.18, 0.67)	38	[176]
DtCzB-PPm	474	96	86.5	0.11	508	28.6	(0.16, 0.66)	33	[176]
DtCzB-CNPm	481	93	524.3	0.15	540	25.0	(0.35, 0.63)	44	[176]
BN-CP1	490	93	79.6	0.12	496	40.0	(0.09, 0.50)	25	[178]
BN-CP2	490	91	83.6	0.13	497	36.4	(0.10, 0.53)	26	[178]

S-Cz-BN	490	94	69.6	0.15	488	30.5	(0.12, 0.43)	26	[179]
D-Cz-BN	490	98	76.0	0.13	488	37.2	(0.11, 0.43)	24	[179]
SF3BN	493	90	26.0	0.15	496	32.2	(0.09, 0.52)	30	[180]
SF1BN	493	93	9.5	0.13	492	35.9	(0.08, 0.47)	28	[180]
BN-TP	523	96	44	0.14	528	35.1	(0.26, 0.70)	36	[181]
(*R*/*S*)-OBN-4CN-BN	500	96	97.4	0.13	508	24.7	(0.16, 0.66)	33	[182]
(*R*/*S*)-OBN-2CN-BN	493	99	95.3	0.12	496	29.8	(0.13, 0.53)	33	[182]
DCzBN-Au	508	95	4.3	0.13	510	35.8	(0.16, 0.67)	34	[183]
(IPr)AuBN	515	92	5.5	0.08-0.09	509	24.0	(0.16, 0.66)	35	[184]
(BzIPr)AuBN	511	86	6.9	0.08-0.09	506	30.3	(0.16, 0.68)	34	[184]
(PyIPr)AuBN	511	93	7.3	0.08-0.09	515	24.0	(0.22, 0.67)	39	[184]
(PzIPr)AuBN	510	78	6.5	0.08-0.09	512	27.6	(0.18, 0.69)	37	[184]
(BzIPr)AuBNO	471	89	27.0	0.11	-	-	-	-	[184]
BNCz-pTPA	487	95	24.0	0.11	496	27.3	(0.12, 0.54)	34	[185]
BNCz-mTPA	489	92	29.4	0.12	496	24.6	(0.11, 0.53)	31	[185]
BN-R	624	94	71.8	0.11	617	22.0	(0.66, 0.34)	47	[186]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, (g) CIE coordinate, and (h) FWHM of electroluminescence.

Table S9 Summary of photophysical properties and device performance of TADF emitters from transition-metal-catalyzed oxidative couplings between C(sp^2)−H and X−H bond

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
SFI23pTz	432	70	97.2	0.40	476	17.3	(0.15, 0.22)	[191]
SFI23mTz	451	35	176.6	0.30	484	16.5	(0.15, 0.27)	[191]
SFI23pPm	414	72	~189	0.36	-	5.1	(0.15, 0.10)	[192]
SF23oTz	473	52	4.3	0.08	484	19.6	(0.19, 0.35)	[193]
(*S*/*R*)-CzpPhTRZ	470	70	65	0.16	480	17.0	(0.17, 0.25)	[194]
B^2TPNF_2	527	29	2.17	0.00	-	-	-	[123]
B^2CNPyF_2	488	23	1.84	0.22	-	-	-	[123]
4hc	460	6	-	0.07	-	~1.2	-	[199]
4ic	466	7	-	0.07	-	1.5	-	[199]
DPS-BDMAC	481	69	2.1	0.02	498	12.4	(0.23, 0.40)	[200]
TRZ-BDMAC	510	87	2.8	0.01	516	13.9	(0.27, 0.51)	[200]
BPO-BDMAC	516	89	3.0	0.03	522	22.5	(0.29, 0.54)	[200]
DCz-ND	475	46	6.0	0.12	469	18.1	(0.15, 0.21)	[204]
DCz-ND-Cz	471	74	4.4	0.13	468	20.8	(0.16, 0.21)	[204]
DCz-ND-DCz	768	72	7.0	0.13	464	20.8	(0.16, 0.20)	[204]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S10 Summary of photophysical properties and device performance of TADF emitters from directed C−H borylation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
fppyBTPA	494	72	2.0	~0	-	20.2	-	[213]
dfppyBTPA	490	95	2.4	~0	-	26.6	-	[213]
fppyBCzP	450	16	0.29	0.24	-	-	-	[213]
dfppyBCzP	455	15	0.18	-	-	-	-	[213]
MeFAC-B	504	97	0.06	7.1	494	22.7	(0.20, 0.42)	[214]
PyB	599	33	2.8	-	-	-	-	[215]
PyB-F	604	28	1.5	-	-	-	-	[215]
BS	526	11	2.7	-	-	-	-	[215]
3-BPh_2	666/704	< 1	1	-	-	-	-	[216]
2-NPh_2	544	4	-	-	-	-	-	[216]
BO2	470	28	140	0.30	471	5.2	(0.16, 0.22)	[220]
BS2	491	81	22	0.12	489	20.9	(0.17, 0.39)	[220]
BO1	458	53	12	0.06	462	12.8	(0.15, 0.15)	[220]
m[B-N]N1	483	91	128.1	0.15	479	36.0	(0.12, 0.27)	[221]
m[B-N]N2	491	90	136.2	0.13	485	33.4	(0.11, 0.32)	[221]
p[B-N]O	497	91	-	0.44	493	26.3	(0.16, 0.51)	[222]
p[B-N]NO	529	89	-	0.37	525	27.6	(0.31, 0.65)	[222]

p[B-N]N	552	83	-	0.32	552	24.6	(0.41, 0.57)	[222]
*t*Ph[BN]	467	75	-	0.63	463	6.1	(0.14, 0.20)	[223]
Cz[BN]	478	72	-	0.57	474	7.1	(0.14, 0.29)	[223]
3B4N	428	91	138.3	0.27	-	-	-	[224]
4B6N	459	100	639.7	0.25	-	-	-	[224]
5B8N	480	91	387.4	0.21	-	-	-	[224]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S11 Summary of photophysical properties and device performance of TADF emitters from one-shot borylation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_max[f] [%]	CIE[g] (x, y)	FWHM[h] (nm)	Ref.
B2	455	53	30.4	0.19	460	18.3	(0.13, 0.11)	37	[225]
B3	441	33	-	0.15	-	-	-	-	[225]
B4	450	57	-	0.15	-	-	-	-	[225]
ν-DABNA	467	90	4.1	0.017	469	34.4	(0.12, 0.11)	18	[226]
α-3BNOH	395	-	260	0.22	-	-	-	-	[227]
α-3BNMes	442	63	9.08/ 7060	-	443	14.6	(0.15, 0.10)	49	[228]
V-DABNA-Mes	484	80	2.4	0.008 5	480	22.9	(0.09, 0.21)	27	[229]
V-DABNA	473	85	1.5	-	483	26.2	(0.09, 0.27)	17	[230]
V-DABNA-F	459	91	2.1	-	468	26.6	(0.12, 0.10)	15	[230]
NOBNacene	410/430	71	1180	0.30	412	11.2	(0.18, 0.07)	41	[231]
ω-DABNA	509	87	8.95	0.011	512	31.1	(0.13, 0.73)	25	[232]
CzDABNA-NP-M/TB	468	86	106	0.18	-	-	-	-	[233]
Cz2DABNA-NP-M/TB	478	85	19	0.18	477	21.8	(0.11, 0.23)	27	[233]

CzB2-M/TB	491	88	50	0.11	-	-	-	-	[233]
Cz2B2-M/TB	483	88	42	0.11	-	-	-	-	[233]
CzDABNA-NP	461	80	77	0.18	-	-	-	-	[233]
CzDABNA-NP-TB/H	465	82	93	0.18	-	-	-	-	[233]
DABNA-NP-M	460	88	89	0.17	-	-	-	-	[233]
DABNA-NP-TB	453	83	90	0.17	457	19.5	(0.14, 0.11)	33	[233]
CzB2-M/P	504	87	24	0.06	497	26.7	(0.12, 0.57)	29	[233]
BN1	458	91	126.6	0.15	456	30.0	(0.14, 0.06)	24	[234]
BN2	467	93	74.6	0.13	468	32.9	(0.12, 0.10)	22	[234]
BN3	458	98	17.8	0.12	457	36.3	(0.14, 0.07)	21	[234]
*t*DPAC-BN	460	94.4	113.8	0.17	460	21.6	(0.14, 0.09)	28	[235]
*t*DMAC-BN	475	89.7	64.2	0.15	472	22.3	(0.12, 0.19)	34	[235]
TPD4PA	445	88.1	4.7	0.05	455	30.7	(0.14, 0.06)	29	[236]
^{t}Bu-TPD4PA	451	90.3	5.6	0.06	460	32.5	(0.14, 0.07)	29	[236]
PTZBN2	483TOL	95	22.4	0.15TOL	478	34.8	(0.15, 0.29)	48	[237]
PTZBN3	468TOL	98	26.5	0.17TOL	468	32.0	(0.15, 0.24)	46	[237]

t-DAB-DPA	446	94	28.8	0.10	459	27.6	(0.14, 0.08)	26	[238]
*m*BP-DABNA-Me	467	97	64.5	0.128	468	24.3	(0.12, 0.14)	28	[240]
*p*BP-DABNA-Me	462	98	53	0.176	464	23.4	(0.13, 0.09)	23	[241]
DPMX-CzDABNA	481	94.2	14.8	0.11	484	27.4	(0.10, 0.32)	29	[242]
C-BN	454	98	64.8	0.21	453	26.6	(0.14, 0.07)	25	[243]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, (g) CIE coordinate, and (h) FWHM of electroluminescence.

Table S12 Summary of photophysical properties and device performance of TADF emitters from free-radical-involved C−H transformations

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
PHzBCO	524	52	9.3	0.006	520	19.6	(0.32, 0.50)	[245]
TRZ-Ph	491	95	4.6	0.03	490	22.6	(0.19, 0.40)	[247]
TRZ-Bu	463	73	51	0.19	466	7.4	(0.16, 0.21)	[247]
Pm-Ph	463	86	55	0.20	470	9.4	(0.15, 0.23)	[247]
IP-6-TPA	600	70	12.4	0.08	-	9.0	(0.51, 0.49)	[249]
IP-9-TPA	600	35	95.4	0.11	-	4.9	(0.51, 0.48)	[249]
AZA-BN	522	94	160	0.18	528	25.7	(0.28, 0.69)	[250]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S13 Summary of photophysical properties and device performance of TADF emitters from C−H vulcanization and selenidation

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
helicene-BN	520	98	71.8	0.15	523	31.5	(0.26, 0.66)	[257]
PSeZTRZ	-	86	-	0.05	-	16.9	-	[259]
SeDF-G	-	7.6	18.5	0.08	-	30.8	(0.31, 0.53)	[260]
SeDF-B	-	8.5	3.9	0.15	-	25.8	(0.19, 0.16)	[260]
SeDF-YG	-	2.6	4.6	0.15	-	23.9	(0.37, 0.51)	[260]
PSeBz	510	-	-	-	510	-	-	[261]
oPSeZBN	-	3	-	0.00	-	-	-	[262]
BNSSe	520	99	12.7	0.12	515	35.7	(0.37, 0.51)	[263]
BNSeSe	514	100	9.9	0.14	512	36.8	(0.37, 0.51)	[263]
BN-Se	502	99	5.2	0.08	506	32.6	(0.15, 0.62)	[264]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S14 Summary of photophysical properties and device performance of TADF emitters from C−H bond transformation-involved umpolung reactions

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
DDCzIPN	477	91	2.8	0.13	497	18.9	(0.22, 0.46)	[268]
DDTPAIPN	543	93	1.5	0.17	528	16.9	(0.30, 0.61)	[269]
DTPAmCPIPN	566	100	1.7	0.15	544	19.2	(0.38, 0.57)	[269]
DDmCPIPN	535	76	2.1	0.13	532	15.7	(0.37, 0.57)	[269]
TXO-TPA	630	83	51.8	0.05	552	18.5	(0.45, 0.53)	[271]
TXO-PhCz	580	90	87.3	0.07	-	21.5	(0.31, 0.56)	[271]
CzTXO	-	30	1860	0.10	-	11.2	(0.16, 0.20)	[272]
CzSOXO	-	51	14.3	0.05	-	13.6	(0.37, 0.57)	[272]
MTXSFCz	451	-	45.3	0.19	-	-	-	[273]
TXO1-TPA	565	25	2.5	0.29	-	-	-	[274]
DTXO-TPA2	569	70	30	0.10	588	25.0	(0.51, 0.48)	[275]
DTXO-PhCz2	537	54	23	0.15	548	15.7	(0.41, 0.55)	[275]
P1	532	72	29.5	0.08	568	5.4	(0.45, 0.53)	[276]
P2	535	55	19.6	0.06	568	3.0	(0.46, 0.53)	[276]
QBP-DMAC	498	78	1870	0.33	523	18.8	(0.30, 0.53)	[278]
QBP-PXZ	535	65	2.3	0.06	550	16.6	(0.41, 0.55)	[278]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.

Table S15 Summary of photophysical properties and device performance of TADF emitters from other novel C−H bond transformations

Compound	λ_{FL}[a] [nm]	PLQY[b] [%]	τ_d[c] [μs]	ΔE_{ST}[d] [eV]	λ_{EL}[e] [nm]	EQE_{max}[f] [%]	CIE[g] (x, y)	Ref.
D2T-TRZ	493	99	2.1	0.01	500	27.1	(0.22, 0.46)	[279]
2S-TRZ	507	99	2.4	0.03	-	35.6	-	[159]
IT-TRZ	505	98	2.2	0.03	-	36.1	-	[159]
IA-TRZ	517	96	2.4	-0.02	-	32.0	-	[159]
D2Y-TRZ	491	71	86	0.41	-	16.4	(0.22, 0.47)	[281]
p-D2T	514	99	2.4	0.14	496	25.6	(0.20, 0.45)	[282]
m-D2T	514	81	1.6	0.12	492	22.3	(0.20, 0.43)	[282]
c-D2T	504	88	2.4	0.17	484	26.3	(0.17, 0.35)	[282]
QAc-TRZ	494	97	3.4	0.08	-	37.3	-	[283]

(a) The λ_{PL}, (b) PLQY, (c) τ_d, and (d) ΔE_{ST} value in solution or film state. (e) The λ_{EL}, (f) EQE_{max}, and (g) CIE coordinate of electroluminescence.